

**REPORT ON THE STUDY OF
THE ION CHROMATOGRAPHIC SYSTEMS IN
THE WATER QUALITY SECTION**

Frank B. Lo

**Ontario Ministry of the Environment
Laboratory Services Branch**

December, 1990

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1. Introduction

The foundation of Ion Chromatography (IC) in the Water Quality Section (WQS) was laid in 1977. At present, the IC Laboratory is equipped with five Laboratory Information System (LIS) Workstations and two additional ion chromatographs for research and development work.

The Dionex Model 10, one of the "non-LIS" instruments was set up and used to conduct experiments to gain an in-depth knowledge of the chemistries, instrumentation and electronic data processing for the separation of chloride, nitrate and sulfate, as practised in the WQS.

This report is organized into four main sections:

- Description of the Chemistries in ion chromatography and study of the effects of changes in the eluent concentration on the chromatographic performance in Section 2.
- Comprehensive review of the ion chromatographic equipment in Section 3.
- Treatment of the chromatographic information by electronic data processing in Section 4.
- Evaluation of the ion chromatographic systems in Section 5.

2. Chemistry

2.1 Ion Chromatography

Chromatography refers to a group of physico-chemical separation techniques based on the differential distribution of solutes between a stationary phase and a mobile phase. The various types of chromatography are classified according to the nature of the two phases involved. When coupled with an appropriate detector, the chromatograph becomes a useful analytical instrument for separation and quantification.

The discovery of chromatography has been credited to Tswett, a Russian biochemist, for his work on the separation of plant pigments using a solid stationary phase (powdered calcium carbonate) with a liquid mobile phase (petroleum ether), and the interpretation of the chromatographic process in 1903. He named the procedure chromatography in 1906 because the plant pigments were observed as bands of characteristic colour. He was the first practitioner of Liquid Chromatography (LC). Modern LC makes use of pressurized mobile phase, efficient columns and on-line detectors. The separation power is much greater and hence it is called High Performance Liquid Chromatography (HPLC).

IC is a branch of HPLC in which the ionic components of a sample mixture possess different attractions (affinities) to the ion exchange functional groups of the stationary phase (column packing, resin) and the mobile phase (eluent). Except for the unretained component, a constant dynamic equilibrium exists for the ions between the stationary phase and the mobile phase. In a system where only a single mobile phase (isocratic elution) is used, the elution force on the ions is the same while the extent of the attraction (retention) exerted by the stationary phase varies. If a component has a stronger attraction with the stationary phase, it is retained longer. Hence, it has a longer retention time. Conversely, if a component has a weaker affinity for the stationary phase, its retention time is shorter. This phenomenon is occasionally referred to as the "race-track effect". The horse (ion) more suited to run on the muddy track (wet column) will arrive at the finish line (detector) earlier.

Therefore, based on this differential affinity, the ions migrate through the column at different rates, producing a series of bands (zones). The bands are detected and displayed as peaks on a recorder chart (chromatogram). The time between injection and the top of the peak is the retention time. The identity of each ion is established by comparing its retention

time with a standard. Its concentration is obtained by comparison with a calibration curve based on either peak height or peak area.

Modern IC, as a novel analytical method for the separation of ions and the subsequent removal of non-analyte ions by the stripper (suppressor) column, was pioneered by Small, Stevens and Bauman in 1975⁽¹⁾. Unlike classical column IC, the method described automatic injection of small sample volumes in μL , used high efficiency separator columns with small resin beads of low capacity, and permitted automatic on-line detection with conductimetry.

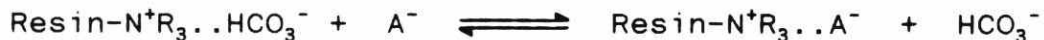
2.2 Ion Chromatography in the Water Quality Section

The ion chromatographic conditions, as practised in the IC Laboratory for the separation of chloride, nitrate, and sulfate, are based on the unpublished work of Chang in 1978⁽²⁾. Briefly, the column is packed with an anion exchange resin developed by Small et al⁽¹⁾. The eluent is a bicarbonate and carbonate buffer solution. The chemical suppressor, either a fibre-suppressor⁽¹⁰⁾ or an anion micro-membrane suppressor, removes the sodium ions from the eluate and replaces it with hydrogen ions. The separated ions are detected as the more conductive inorganic acids in a dilute carbonic acid stream.

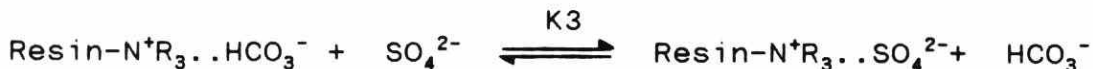
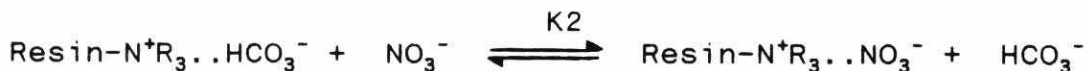
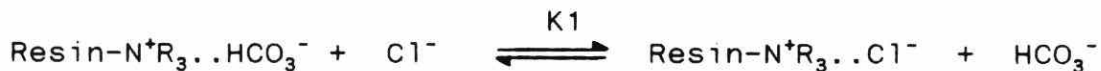
An evaluation of the Dionex ion chromatographic systems at the earlier stages of development of the technique, subsequent modifications, and some applications notes have been reported by Crowther et al⁽³⁻¹⁰⁾. The chemistries in the column between the stationary phase and mobile phase, and in the suppressor between the eluate and regenerant will be explained in Sections 2.2.1 and 2.2.2 respectively. Resolution, an evaluation of the separation power of the chromatographic system, based on a mathematical equation is introduced in Section 2.2.3. The effects on the chromatographic performance at various eluent concentrations will be presented in Section 2.4. A detailed discussion of the major components of the entire ion chromatographic system and their functions will be reserved for Section 3 - Instrumentation.

2.2.1 Chemistry in the Column

The affinity of an ion (A^-) in the stationary phase ($\text{Resin-N}^+\text{R}_3$) and the mobile phase (HCO_3^-) equilibrium is given by:



In a mixture of chloride, nitrate and sulfate, the three equilibria are given by:



(.. means attraction between the ions).

In an ion chromatographic system, if $K_1=K_2$, there is no separation between chloride and nitrate. Similarly, if $K_2=K_3$, nitrate and sulfate are not separable. If K_1 is smaller than K_2 and K_3 , chloride will be eluted first. Its retention time is shorter. In the choice of bicarbonate and carbonate eluent, the equilibrium constants are in this order- $K_1 < K_2 < K_3$. Therefore the separation of chloride, nitrate and sulfate is possible and follows the same order.

The bicarbonate is primarily a pusher for mono-valent ion. Even though sulfate can be eluted by bicarbonate, the carbonate acts as the di-valent pusher.

2.2.2 Chemistry in the Suppressor

In his fundamental work in 1975, Small used a suppressor column to achieve two objectives necessary for the successful utilization of conductivity detection. The latest design, a more efficient micro-membrane suppressor was used in this study. First, the suppressor exchanges the sodium ions from the eluate for protons through an ion exchange membrane into the weakly dissociated carbonic acid. In this process, the conductivity of the bicarbonate and carbonate is reduced from about 600-1000 $\mu\text{S}/\text{cm}$ to approximately 10-20 $\mu\text{S}/\text{cm}$ as the carbonic acid. The background conductivity is reduced with the concomitant reduction in baseline noise⁽¹³⁾.



Second, the suppressor converts the chloride, nitrate and sulfate of sodium into its corresponding acids.



As the result, these strong mineral acids are detected as highly conductive ions in the presence of only weakly conductive carbonic acid. Together these two effects significantly improve the signal to noise ratio and, consequently, greatly enhance the detector sensitivity.

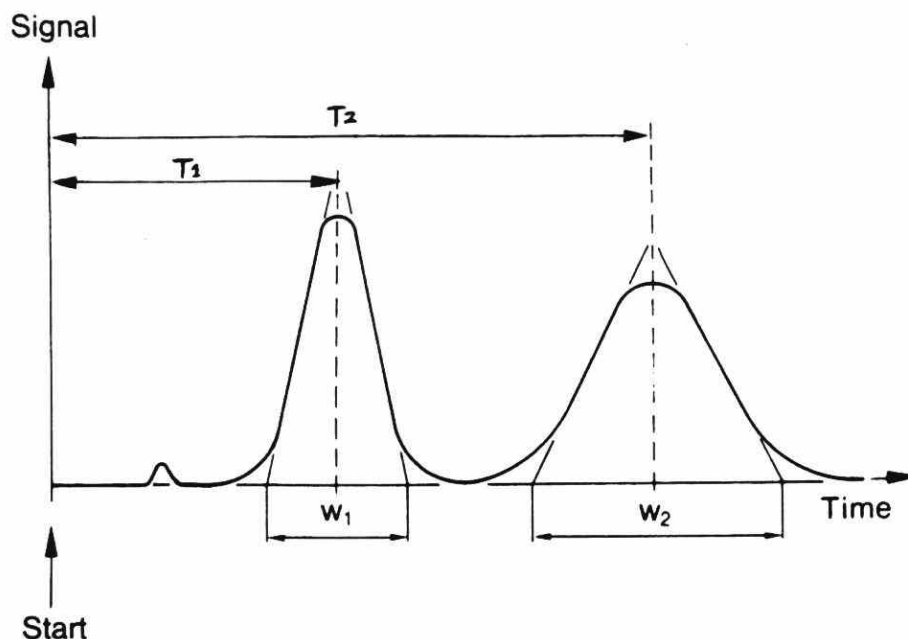
2.2.3 Resolution

The separation of ions is achieved by the proper choice of columns and eluents⁽¹¹⁻¹²⁾. In other words, the chemistries in the column produce the separation. The extent of the separation is expressed as resolution (R_s). It measures the amount of band broadening of the peak and is mathematically expressed as:

$$R_s = \frac{2 (T_2 - T_1)}{W_1 + W_2}$$

where T_1 : Retention time of the earlier peak.
 T_2 : Retention time of the later peak.
 W_1 : Peak width of the earlier peak at its base.
 W_2 : Peak width of the later peak at its base.

On the chromatogram they are represented as:



T_1 , T_2 , W_1 and W_2 must have the same units either in time or distance on the chart. For two adjacent peaks which are symmetrical and have equal response, they can be seen as distinct if the R_s is 0.5. If R_s equals 1.0, they are 98% separated. If R_s equals 1.5, they are baseline resolved (completely separated) and in preparative chromatography, this degree of resolution is necessary. For analytical chromatography, R_s of 1.0 is sufficient for accurate and reproducible quantification. Any effort trying to increase the R_s to larger than 1.5 is unnecessary because it leads to long analysis time.

2.3 Experimental

2.3.1 Instrument

The instrument used in this series of studies was the Dionex Model 10 ion chromatograph. It is equipped with the following components.

- 2.3.1.1 Eluent delivery pump: Single piston Mini-pump (Operating flow rate at 0.77 to 7.7 mL/min), Milton Roy Co., Laboratory Data Control Division.
- 2.3.1.2 Pressure gauge: (Maximum pressure at 2000 psi), Dionex Corp.
- 2.3.1.3 Injector: Air-operated pneumatic 6-port valve, Valco Instruments Co. Inc.
- 2.3.1.4 Pneumatic valve: 3/64 psi, Skinner Electric Valve Division.
- 2.3.1.5 Guard column: One 5-cm HPIC-AG1, Dionex Corp.
- 2.3.1.6 Separator column: Two 5-cm HPIC-AG3, Dionex Corp.
- 2.3.1.7 Suppressor: Anion micro-membrane suppressor, AMMS-1, maximum eluent flow rate at 3.0 mL/min, Dionex Corp.
- 2.3.1.8 Detector: Multi-range conductivity detector, Dionex Corp.

2.3.2 Accessories

- 2.3.2.1 Proportioning pump: AutoAnalyzer I, Technicon Instrument.
- 2.3.2.2 Integrator: Model 4270, Varian.
- 2.3.2.3 Recorder: Dual pen chart recorder, Model 585, Linear Instrument Corp.
- 2.3.2.4 Syringe: Disposable plastic 10 cc graduated syringe with Luer tip.

- 2.3.2.5 Air cylinder: Compressed cylinder of dry air, Matheson Gas Products Canada.
- 2.3.2.6 Pipettes: Volumetric, various sizes as required.
- 2.3.2.7 Volumetric flasks: Various sizes as required.
- 2.3.2.8 Conductivity meter: CDM 83 Conductivity Meter, Radiometer.
- 2.3.2.9 pH meter: PHM 84 Research pH Meter, Radiometer.

2.3.3 Reagents

The reagents and standard solutions were prepared with deionized distilled water (DDW) of less than 1 $\mu\text{S}/\text{cm}$ conductivity. The glassware was cleaned with 4% (v/v) dilute hydrochloric acid and thoroughly rinsed with DDW.

- 2.3.3.1 Sodium chloride (NaCl): Anhydrous analytical grade.
- 2.3.3.2 Potassium nitrate (KNO_3): Anhydrous analytical grade.
- 2.3.3.3 Sodium sulfate (Na_2SO_4): Anhydrous analytical grade.
- 2.3.3.4 Sodium bicarbonate (NaHCO_3): Anhydrous reagent grade.
- 2.3.3.5 Sodium carbonate (Na_2CO_3): Anhydrous reagent grade.
- 2.3.3.6 Sulfuric acid (H_2SO_4): Concentrated reagent grade.
- 2.3.3.7 Calibration Stock Solution (400 mg/L as Cl,
400 mg/L as N and
2000 mg/L as SO_4):
0.6594 g sodium chloride, 2.8876 g potassium nitrate and 2.9576 g sodium sulfate were accurately weighed and transferred into a 1 L volumetric flask. They were dissolved and diluted to the mark with DDW.
- 2.3.3.8 Calibration Intermediate Solution (40 mg/L as Cl,
40 mg/L as N and
200 mg/L as SO_4):
100 mL of the Stock Solution was pipetted into a 1 L volumetric flask and diluted to the mark with DDW.

- 2.3.3.9 Test Solution (1.2 mg/L as Cl,
1.2 mg/L as N and
6.0 mg/L as SO₄):

30 mL of the Intermediate Solution and 10 mL of the Stock Eluent were pipetted into a 1 L volumetric flask and diluted to the mark with DDW.

This solution contained the same amount of sodium bicarbonate and sodium carbonate as the working eluent. Therefore, by matching the ionic strength of the two solutions, the negative response of the water peak on the chromatogram was eliminated. Otherwise, the water dip might interfere with the integration of the closely eluting chloride peak.

- 2.3.3.10 Stock Eluent (0.3 M NaHCO₃ and 0.24 M Na₂CO₃):

25 g NaHCO₃ and 25 g Na₂CO₃ were weighed on a top-loading balance and transferred to a 1 L volumetric flask. They were dissolved and diluted to the mark with DDW.

- 2.3.3.11 Working Eluent: Eluent of various concentrations were prepared by diluting aliquots of the Stock Eluent to 1 L with DDW as follows. Sufficient amounts were prepared to fill a 4 L plastic container. The eluent concentrations in the table below are expressed as percent of the "regular concentration" used for routine IC.

% of Regular Concentration	mL of Stock Eluent	Eluent Concentration	
		M NaHCO ₃	M Na ₂ CO ₃
80	8.0	0.00240	0.00192
85	8.5	0.00255	0.00204
90	9.0	0.00270	0.00216
95	9.5	0.00285	0.00228
100*	10.0	0.00300	0.00240
105	10.5	0.00315	0.00252
110	11.0	0.00330	0.00264
115	11.5	0.00345	0.00276
120	12.0	0.00360	0.00288

* Eluent used for routine analyses.

2.3.3.12 Regenerant (0.025 N H_2SO_4): 7 mL of concentrated sulfuric acid was diluted to 10 L with DDW in a collapsible plastic container.

2.3.4 Operating Parameters of the Ion Chromatograph

Instrument: Dionex, Model 10.
Sample: 1.2 mg Cl/L, 1.2 mg N/L, and 6.0 mg SO_4 /L.
Sample volume: 0.2 mL.
Columns: One Dionex AG1.
Two Dionex AG3.
Eluent: 0.003 M NaHCO_3 and 0.0024 M Na_2CO_3
at 2.5 mL/min.
Suppressor: Anion micro-membrane suppressor, Dionex
AMMS-1.
Regenerant: 0.0025 N H_2SO_4 at 4.0 mL/min.
Detector: Conductivity at 10 $\mu\text{S}/\text{cm}$ full scale.
Integrator: Varian, Model 4270.
Mode: Peak height.
Attenuation: 256.
Chart speed: 1 cm/min.

2.4 Results and Discussion

2.4.1 Chromatography Using Standard Operating Conditions

Three chromatograms were obtained to establish the performance of the ion chromatographic system. An example is given in Figure 1. The data of retention times of chloride, nitrate and sulfate, and their peak height responses are given in Table I.

The peak at 1.1 minute is due to bicarbonate while the retention times for chloride, nitrate and sulfate are about 2.4, 7.4 and 10.8 minutes respectively. The nitrate and sulfate peaks are closely eluted but they are baseline-resolved. Their resolution will be calculated to evaluate the efficiency of the system in Section 2.4.4. The precisions are below 1 %RSD for retention times and about 2 %RSD for peak responses.

The sulfate peak is quite symmetrical. Excessive tailing indicates poor choice of column and/or eluent. If the system has been properly evaluated, such as what is presently in use in the IC Laboratory, peak tailing signifies contamination of the column(s) or suppressor.

2.4.2 Effect of Eluent Concentration on Conductivity and pH

The conductivities of the eluent at various concentrations were measured at the Radiometer conductivity meter and the pH values were obtained from the Radiometer pH meter. The results are shown in Table II. The relationship between the eluent concentrations and conductivities was plotted in Figure 2. As expected, the conductivity increases as the concentrations of sodium bicarbonate and sodium carbonate increase. The relationship in this range is linear with a correlation coefficient of 0.9996 and a slope of 6.97.

The pH remains stable at about 10. This lack of significant change is predictable because the bicarbonate and carbonate are conjugate bases of the weak carbonic acid. This fact is crucial in the choice of a suitable eluent for an ion chromatographic application. The pH of the eluent determines the retention times of ions and their elution order⁽¹¹⁾. When the components are well separated a reproducible chromatogram makes peak identification and quantification easy. This feature is important in the operation of the WQS which deals with large number of samples throughout the year.

2.4.3 Effect of Eluent Concentration on Eluate Conductivity

After passing through the suppressor, the eluent is called the suppressed eluate⁽¹³⁾. It is mainly dilute carbonic acid as explained in Section 2.2.2. The conductivity reading of the eluate at various concentrations were recorded from the Dionex detector. Furthermore, the eluates were also collected and their conductivities measured at the Radiometer conductivity meter. The results are given in Table III and shown in Figure 3. The concentration of carbonic acid is calculated from the molar equivalents of the bicarbonate and carbonate, and based on complete conversion.

An examination of the data revealed that the conductivity readings obtained from the Radiometer conductivity meter at 25°C were higher than those from the Dionex detector. This is because the Dionex instrument was operating at ambient temperature of 22.2°C. Nevertheless, both sets of data show linear relationship. It is worthwhile noting that the conductivity reading of 12.7 $\mu\text{S}/\text{cm}$ for the eluate of 100% regular concentration agrees with the value of 12 $\mu\text{S}/\text{cm}$ reported earlier by Crowther et al⁽¹⁰⁾.

On the whole, the conductivities of the suppressed eluate in the investigated range of eluent concentrations were quite low. This demonstrates the effectiveness of the chemical suppression. A change of up to 20% in the eluent concentration will not affect the sensitivity of the detector.

2.4.4 Effect of Eluent Concentration on Retention Time and Resolution

Chromatograms of chloride, nitrate and sulfate were obtained at various eluent concentrations (80%, 85%, 90%, 95%, 100%, 105%, 110%, 115% and 120% of regular concentration). They are shown in Figures 4.1 to 4.9 respectively. The data of retention times and resolution are given in Table IV. Each retention time reported is the average of three injections. The resolution was obtained from the last of the three chromatograms and the measurements were based on chart distance in centimeters.

As the concentrations of the bicarbonate and carbonate increased, the strength of the eluent increased. The resulting effect was shorter retention times for the ions.

This trend is plotted in Figure 5. The amount of decrease is most significant for sulfate. If the eluent strength is increased further, it is predictable that the elution order for nitrate and sulfate will be reversed. However, this should not pose any concern to us since an increase of the eluent strength by more than 20% is not expected to be necessary.

The relationship between eluent concentration and resolution is shown in Figure 6. Only the resolution between nitrate and sulfate was calculated because of two reasons. First, the chloride peak is well separated from nitrate but the nitrate and sulfate peaks are closely eluted. Second, the effect of eluent strength on retention time is the strongest on sulfate and consequently the effect on the resolution between nitrate and sulfate will be stronger. At 100% of regular concentration the resolution between nitrate and sulfate is slightly larger than 1.75. If only baseline-resolution is desired, the concentration can be increased to 112% of regular strength. By doing so, the analysis time is reduced from 9 to 8 minutes (Figure 5). This time saving of 11% is an important characteristic which gives us an option to increase the sample throughput when the performance of the ion chromatograph is optimal.

3. Instrumentation

Chromatography is classified under instrumental analytical techniques. The various components, when selectively and appropriately put together, will produce the separation, quantify the peaks and manipulate the data.

In the earliest form of IC⁽¹²⁻¹³⁾, the ion exchange resin was placed in a glass column. The eluent was added continually from the top and gravity provided the driving force for the elution. The sample was manually deposited on the top of the column. Fractions of the effluent were collected at the bottom in beakers and taken for assay by other means. Not only were such procedures laborious and time consuming, the separation was poor. The high capacity of the resin required large sample sizes and the resin had a narrow useful pH range.

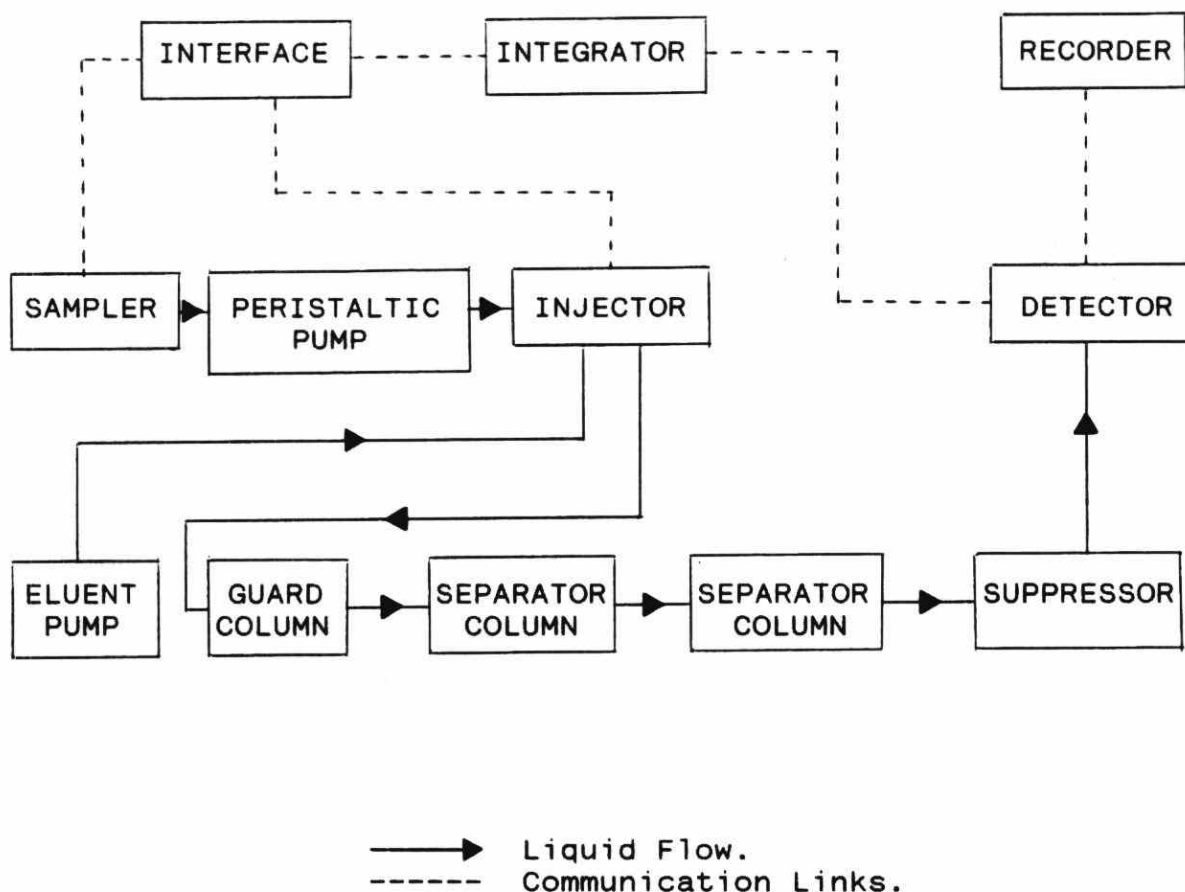
Modern IC, so popularly used in analytical laboratories, is the result of the following two important developments: first--synthesis of the ion exchange resin, and second--direct coupling of a detector to the column.

The synthesis of ion exchange resin was demonstrated by Adams and Holmes⁽¹⁴⁾ to be possible by forming cross-linked and insoluble polymers in 1935. This led to the eventual preparation of porous and pellicular resins with controlled diameters of the resin bead, thickness of the pellicular layer, and capacity of the stationary phase. An ion exchange column was used by Marinsky et al to separate radioactive species and was coupled directly to radiometric detectors in 1947⁽¹⁵⁾. This was the first ion chromatograph with an on-line detector. Using the same principle, Moore and Stein performed the first automated detection of amino acids in 1948⁽¹⁶⁾.

The use of IC for the analysis of inorganic ions became possible in 1971 when the conductimetric detector was developed⁽¹³⁾ at Dow Chemical Company. Small et al published their landmark paper on eluent suppression by chemical means in 1975⁽¹⁾. Dionex Corporation, after being granted a licence for the chemical suppression technique, manufactured and marketed the first instrument in the same year and named the technique "ion chromatography". Later, demand for ion separation grew and other chromatography instrument companies became involved with the commercialization of the "non-suppressed" approach. This technique of using electronic means to zero out the conductance of the eluent is also known as non-chemical suppression ion chromatography or single-column ion chromatography (SCIC) as opposed to the dual columns in chemical suppression. Some of these notable companies include Alltech Associates Inc., Interaction Chemicals Inc., Metrohm Ltd., Shimadzu Scientific Instruments, Inc., Varian Canada Inc., Waters-Millipore Corp., and Wescan Instruments, Inc.

Because of the acceptance of both techniques - chemical suppression and electronic suppression, the term "ion chromatography" now includes any chromatographic method applied to the determination of ions. However, when the WQS set up its IC in 1977, Dionex was the only supplier of equipment and accessories. For this reason, we are using chemical suppression and its significance will be discussed in Section 3.7.

The major components of our ion chromatographic systems are - eluent pump and pressure gauge, sampler, peristaltic pump, injector, interface, columns, suppressor, detector, integrator, and recorder. Their lay out is shown in the following diagram.



The IC laboratory has acquired the following six ion chromatographs:

A. Model 10 - 2 units.

This is the first ion chromatograph produced by Dionex and is therefore the oldest single channel instrument in our laboratory. It was designed to house the suppressor column in addition to the other indispensable components. During analysis, the eluent is pumped through the column and the suppressor column. However the suppressor column must be regenerated and rinsed periodically. Therefore, switching valves controlling the flows of the eluent, regenerant and DDW were included. Compartments were provided for containers of eluent, regenerant and DDW. For these reasons, this model is the largest in size. One unit is used for workstation "ORGSO4" and another is used for development work (see Section 2.3.1).

B. Model 16 - 1 unit.

The components of this model are the same as the Model 10 except that two sets are installed. This instrument is applied to the "double channel" analysis of air sampling filters at "PRLOV/PRSEQ".

C. Model QIC - 2 units.

This is also a single channel instrument like the Model 10 but it is down-sized because replacing the suppressor with the fibre suppressor has eliminated the need for some of the switching valves. Spaces for liquid containers are not provided. One unit is used for "RMDSO4" and another for "PRIC1".

D. Model 4000i - 1 unit.

Dionex produced this latest model to take advantage of automatic electronic control of switching valves and enable chromatographers to perform gradient elution. Some of the main features are:-

- dual piston reciprocating pump.
- electronic pressure sensor.
- switching valves for selection of 6 eluents.
- programmable flow rate.
- gradient elution capability.
- hardware for 4 channels.
- higher operating pressure to 4000 psi.
- conductivity detector with adjustable temperature compensation.

3.1 Eluent Pump, Pressure Monitor and Tubings

The driving force of an ion chromatograph is provided by a liquid pump. It delivers the eluent from a reservoir, through the various components to the detector. Without the dynamic environment provided in a constant flow of fresh eluent, the exchange mechanism within the column would not happen and no separation could be achieved. The pump should produce minimal perturbation in the flow pattern to maintain a fairly stable elution time. To provide reliable service and to minimize contamination to the eluent, the surface of the pump which come in contact with the eluent should be constructed of inert materials. The use of metal parts will result in poisoning of the stationary phase, increase in background noise for electrochemical detectors and making the analysis of metals at trace levels very difficult. The plunger is made from sapphire and the check valves from shock-hardened steel. Other materials used for pump parts include KEL-F, high alumina ceramic, Rulon and stainless steel.

Two types of pumps are used in the IC laboratory.

A. Milton Roy MiniPump, Model 396 - 8 units.

Five are used for the "workstations" and three are used for other purposes such as the conditioning and cleaning of columns and suppressors. One is installed in the spare instrument. The MiniPump is a single piston reciprocating pump. The operating flow rates can be selected between 0.07 and 7.76 mL/min by turning the vernier on the barrel. The settings of 1%, 10% and 100% represent flow rates of 0.07 mL/min, 0.77 mL/min and 7.67 mL/min respectively. The pressure rating is 5000 psi.

B. Dionex pump on Model 4000i - 1 unit.

Some of its main features have been described earlier in Section 3.D. Since it is a dual piston pump, it provides better precision and pulse free flow than a single piston pump. The flow rate can be digitally selected between 0.1 and 9.9 mL/min in steps of 0.1 mL/min. The maximum operating pressure is 4000 psi. An alarm switch ensures that the pressure in the system remains within predetermined minimum and maximum limits. It is possible to choose any of six different eluents with pneumatically operated valves.

Both types of pumps are equipped with inlet and outlet check valves to ensure the flow of the eluent in the proper direction. To monitor the back pressure, the Milton Roy MiniPump is connected to a pressure gauge rated at 1000 or 2000 psi while the Dionex 4000i pump is connected to a pressure transducer which depicts the pressure on a light emitting diode.

Teflon tubing (0.78 mm ID and 1.56 mm OD) is used to connect the pump, injector, columns, suppressor and detector in series. It is also used for the liquid line between the sampler and the injector.

3.2 Sampler

The sampler holds the plastic tubes into which the aqueous samples are collected for analysis. Even though its function is a simple one, the sampler fulfills an indispensable role by allowing unattended operation during off-duty hours. Therefore during regular working hours, our technical staff can afford the time to set up the equipment, calibrate it and load the sampler. Because of its full automation, the analysis of 100 or more samples a day is attainable. To be dependable the movement of the pipet and the positioning of either the pipet or the sample tubes should be predictable and precise. The laboratory uses two types of sampling devices.

A. Gilson Sampler, Model SC15/TD15T - 2 units.

The pipet (probe) is made from stainless steel and the sampling tube from Teflon. The sample tubes are inserted into the spool holder which wraps around and sits on the base. The spool can hold up to 400 tubes of 9 to 15 mL. The sample tube position is advanced by the pulling of the take-up spool holder. The movement of the carousel is triggered by a switch in the "interface" (Section 3.5) and the duration of aspiration is controlled by the "integrator" (Section 3.9). One unit with a capacity of 400 tubes is used for the RMDS04 workstation. The second unit with a capacity of 250 tubes is modified so that a signal from the interface advances the carousel by two positions to be compatible with the double channel workstations of PRLOV/PRSEQ on the Dionex Model 16. Gilson has stopped producing the carousel type sampler.

B. Gilson Sampler, Model 222 - 2 units.

Unlike the above it is an X/Y/Z type sampler. Only the sample probe moves. The destination of its movement is programmable and therefore can be sequential or random according to instructions. In addition, it is designed to accommodate tube sizes of 1 to 20 mL by the selection of different tube racks. The rack we use holds sixty 9 mL (13 x 100 mm) tubes. Up to 5 racks can be placed in the tray. Based on our operation, one tray can hold 120 sample tubes. The two units are used on the PRIC1 and ORGS04 workstations. The pipet arm can be modified to sample two samples at once by using two pipets and by programming its movement to advance two positions.

3.3 Peristaltic Pump

The peristaltic pump is responsible for the following functions.

- supplying the auto-sampler with fresh DDW.
- delivering the sample solution to the injector.
- pumping spiking solution to the sample for matrix matching.
- providing dilution DDW if applicable.
- separating aliquots of serial samples with air bubbles.
- pushing the regenerant through the suppressor.

Since the various functions above require different flow rates, the pump is set at a constant rotating speed and the flow rates are determined with the proper selection of "Tygon" pump tubes according to their inner diameters. Each size is identified with colour codes on the shoulders.

There are two types of peristaltic pumps.

A. Technicon, AutoAnalyzer II - 3 units.

The rotating speed is fixed. The flow rate is based on and proportional to the tubing sizes, and hence it is also known as the "proportioning pump". The tubing holder has grooves for 23 lines. A platform (tray) provides space for other tubings and mixing coils which are necessary for automatic on-line dilution of samples and for flow control of reagents. These units are used at the ORGS04, PRIC1 and PRLOV/PRSEQ workstations.

B. Watson Marlow, Piper Pump - 1 unit.

It is a variable speed peristaltic pump. Since the same pump tubes are used as with the Technicon pump and a faster flow rate is required for the RMDS04 workstation, the pump rotating speed is set the maximum which is two and a half times faster than the Technicon pump. For example, by using a pump tube rated at 2.0 mL/min at the faster speed, the flow rate will be 5.0 mL/min. The Piper Pump can hold 4 tubes which are adequate for this workstation.

3.4 Injector

Before the injector (better known as the injection valve) was invented, the operator had to perform what is known as "stop flow" injection. HPLC practitioners can recall the manual task

of stopping the eluent pump, uncapping the column top, depositing a known volume of sample with a micro-syringe, replacing the cap and restarting the pump. The main difficulties of this method are manual operation and poor precision.

The commercialization of IC instruments began at the time when injection devices were available. The injector is composed of two main parts, the body and the shaft. Holes are drilled on the body and grooves are cut on the shaft. In the "load" position, the eluent passes directly to the column, by-passing the sample loop and at the same time allowing the sample loop to be filled with the sample. In the "inject" position, the shaft is either slid or rotated depending on the construction. In the latter orientation, the eluent passes through the injection loop and carries the sample to the column to be chromatographed.

The sample volume to be injected is determined by the internal volume of the injection loop which is made from Teflon tubing of 0.78 mm ID. The internal volume is proportional to the tubing length. One cm is equivalent to 4.86618 μ L or 1 mL requires 205.5 cm of tubing.

Although the injection valve can be operated manually, pneumatically or electrically, only the air-operated type is used in the IC laboratory. The required pressure of 60 psi is supplied by a compressor or an air cylinder. The position of the shaft is controlled by the direction of the air supply. The solenoids (Skinner valves) control the air flow to the injector. The "integrator" (Section 3.9) controls the timing function for the solenoids which are housed inside the "interface" (Section 3.5).

A. Dionex Injection Valve - 3 units.

The shaft slides from one end of the body to another for "load" or "inject". This device has eight ports and is found on the PRLOV/PRSEQ workstation and in the Model 4000i ion chromatograph.

B. Rheodyne Injection Valve - 1 unit.

It is a conventional 6-port rotary injection valve. One unit is installed at the RMDSO4 workstation.

C. Valco Sample Injector - 3 units.

It is also a 6-port rotary injection valve. They are installed in the Dionex Model 10 ion chromatographs used at workstations ORGSO4 and PRIC1.

3.5 Interface - 4 units.

Of all the major components of an ion chromatographic system, this is the only "WQS-made" device. It contains the infra-red relay switches and the solenoids (Skinner Electrical Valves). From the integrator the interface receives time function signals and triggers the sampler to move to either the "rinse" or "inject" positions, and activates the injector to rotate to either the "load" or "inject" positions. Therefore the "interface" acts as switches on command from the integrator. One unit is used for each of the workstations of ORGS04, PRIC1 and RMDS04.

Two sets of injector switches and solenoids (Humphrey, Model Mini-Myte) are installed on the PRLOV/PRSEQ workstations. Unlike the Skinner Valve with two openings for air, the Mini-Myte has three openings, one for air supply and the other two openings responsible for the inject or load positions of the injection valve. The electrical signals come from the time-functions of the integrator.

The Dionex 4000i comes with its own solenoids. The other Model 10 ion chromatograph has two Skinner valves. Both ion chromatographs are used for special projects and thus do not require any auto-sampler or interface.

3.6 Column

The ion chromatographic column is actually made up of two components - tube and packing. The latter is a slurry of micron size particles which may be organic or inorganic. The organic packing is called the resin. The functional groups (stationary phase) are either an integral part of the particles or are attached to them. The separator column is the "heart" of a chromatograph. The chemistry has been described in Section 2.2.1.

The cylindrical tube is usually 3 mm ID and varies from 5 to 30 cm in length. Made of either stainless steel or plastic, it contains the particles whose surfaces have been modified with the desirable functional group. It is the stationary phase that determines what separation mechanism is operative, and that in turn dictates the choice and composition of the mobile phase and often the selection of the detection mode. Therefore, the column should be correctly referred to as the "ion exchange material" prepared from either the particles or the modified particles.

Ion exchange resins, the column particles in IC, are obtained by co-polymerization of styrene (PS) and divinylbenzene (DVB). The rigidity of the resin bead is controlled by the degree of cross-linking provided by the DVB. Subsequent modification of the PS on the surface produces the desired functional group. This type of resin is called a "superficial" ion exchanger. The efficiency improves as the particle size decreases. Although only the surface is functionalized, this porous material requires large sample sizes and does not favour diffusion in the stationary phase. Small et al⁽¹³⁾ obtained a patent for attaching "colloidal" ion exchange resin (less than 1 micron) of one charge to a much larger substrate particle (around 20 microns) of PS/DVB. This technique is termed "surface agglomeration" or "pellicular" resin. The ratio between the sizes of the substrate and the colloidal particle is about 100. Resins of this type offers these advantages.

1. The column capacity can be controlled through the choice of the size of the colloidal resin and the substrate particle.
2. The degree of cross-linking of the colloidal resin can be controlled, leading to improvement in selectivity and column efficiency.
3. In the manufacturing process, a modest amount of the colloidal resin can be prepared, resulting in reproducible resin properties.
4. The entire substrate particle is covered with colloidal particles. The absence of partially functionalized regions leads to uniform mass transfer in the stationary phase.

In summary, all these factors make it possible to produce on a large scale reproducible columns of much improved peak shape and separation power. Dionex now supplies both anion and cation columns produced by this method.

For the analysis of chloride, nitrate and sulfate, the surface of the PS/DVB bead (substrate) is sulfonated and oppositely charged quaternary ammonium groups (colloidal particles) are attached to these sulfonated groups by electrostatic interaction. A series of eleven columns have been manufactured by Dionex with different specifications regarding substrate diameter, percent cross-linking, column capacity and hydrophobicity.

When a chromatographic separation is attempted, the selection of the column is largely by experimentation. For anions, columns with cationic functional groups are used. The WQS uses Dionex columns which evolved from the pellicular resin reported by Small⁽¹⁾. A train of three columns are connected

in series - one AG1 and two AG3. Each column is capped at both ends with compressed fibrous Teflon frits of 2 μ m pore and 7 mm diameter. The frit at the front end traps any suspended materials and particulates in the many types of and sometimes dirty samples we handle.

The AG1 guard column protects the more expensive separator column from plugging, contamination and poisoning. It is 5 cm long and contains the same ion exchange resin as the 25 cm separator AS1. The particle is 25 μ m diameter with 5.0% cross-linking, and has 30 μ eq/column capacity and medium hydrophobicity. This is the first anion column Dionex produced but has become obsolete because of its long elution time for sulfate (30 minutes on a 25 cm column).

The replacement, AS3, is the first fast separator column of the same specifications. The elution times of chloride, nitrate and sulfate are shorter in this new column. In the IC laboratory, instead of using one 25 cm AS3 column which is a normal arrangement, two 5 cm AG3 columns packed with the same ion exchange resin are installed in series. Even though the use of shorter column is rarely worthwhile, the elution time can be drastically reduced by using two shorter guard columns⁽¹³⁾. It is acceptable if adequate separation can still be achieved with the "two-stage column". This offers us the advantage of reducing the analysis time from about 30 minutes to less than 10 minutes. The increase in sample throughput in our production line operation is significant.

The eluent of sodium bicarbonate and sodium carbonate is adopted from the work of Chang⁽²⁾ who described the various successful applications of IC in environmentally important waters. Using a low capacity pellicular anion exchange column (2.8 mm ID x 50 cm), the anions of chloride, nitrate, phosphate, bromide, nitrate, and sulfate are eluted with 0.003 M sodium bicarbonate and 0.0024 M sodium carbonate in 20 minutes. The concentrations were derived from their peak heights by comparison with external standards.

Column performance will deteriorate due to plugging, contamination and occasional chemical poisoning. Sometimes, some of the column efficiency can be regained by cleaning with dilute hydrochloric acid, methanol and/or acetonitrile. The use of carbonate eluent promotes bacterial growth which physically destroys the resin and such damage is permanent.

All the workstations use the same guard columns (AG1) and separator columns (AG3) which are purchased from Dionex Canada Ltd.

3.7 Suppressor

Immediately following the separator column, the suppressor is a device which exchanges the highly conductive ions in the eluent for hydronium or hydroxide ions. It changes the chemistry of the eluate before it enters the detector so that the end product is dilute carbonic acid if carbonate eluent is used for anion analysis. The chemistry has been dealt with in detail in Section 2.2.2. The fundamental importance of sensitivity enhancement will be explained here.

The magnitude of the noise in the detector signal is proportional to the magnitude of the background signal⁽¹³⁾. In other words, the magnitude of the noise is higher if the background signal of the detector is higher. Therefore, if the background signal is decreased, the noise level will diminish. This is accomplished by reducing the conductance of the eluate. Since the magnitude of the analyte signal is the same in both the non-reduced and reduced background signal, the ratio of analyte signal to noise is favoured by the lowering of the noise which is achieved by the reduction in the background signal. The effect is a significant increase in signal to noise (S/N) ratio - that is improved sensitivity. This is an important consideration in the evaluation of the performance of an ion chromatographic method and especially for trace analysis. Reduction in background signal offers another advantage of wider dynamic range to the detector.

The choice of the regenerant also plays a role in enhancing the sensitivity. In the WQS, sulfuric acid is the regenerant which exchanges hydronium ion for the sodium ion. The analytes of chloride, nitrate and sulfate are converted from the sodium forms to the acid forms which are more mobile and therefore more conductive. The advantages of chemical suppression in IC can be summarized as follow.

1. The background conductance is reduced, thus reducing noise while increasing the linear dynamic range of the detector.
2. The mobility of the analyte ion is increased, thus increasing its response.
3. Both 1 and 2 combine to improve the S/N ratio of the analyte ion.

Small introduced the chemical suppression technique in 1975⁽¹⁾ and Dionex marketed the column (packed bed) suppressor in the same year^(1,3). Without the chemical suppressor, IC could not have become a popular analytical technique for ions with varying degrees of conductance. However the column suppressor has problems. First, it differs in an important way from the

separator column. While the latter, in principle, continues to provide the same separation power regardless of the amount of eluent passed through it, the suppressor column's ability to exchange the undesirable eluent ion is limited. Eventually, it becomes exhausted and must be either regenerated or replaced. Second, the suppressor column does not assist in the separation of the analyte ions and, in fact, the void space and random flow path produce undesirable band broadening. The separated bands become slightly merged and the end result is less peak resolution. Third, if the analyte ion for anion separation forms a weak acid in the suppressor column, a fraction of the analyte will exist as the undissociated species which being uncharged, can readily enter the hydrogen form of the resin phase. It is slightly retained by the suppressor column even though that is not the purposeful function of the latter. As the suppressor is exhausted the retention on the resin will be shorter and the elution volume of the species that form weak acids will be observed to drift to lower value. Peak drift is clearly a nuisance in identification and quantification. Fourth, the "carbonate (water) dip" also drifts as the suppressor column is consumed. When it drifts to an analyte peak such as fluoride or chloride in the carbonate eluent system, the result is problematic.

To overcome the above problems, Dionex produced the fibre suppressor in 1983. While the chemistry is the same, but unlike the suppressor column, this device is based on a new mechanism of using semi-permeable membrane where the undesirable ions may migrate from the eluate to the regenerant side exchanging for the desirable ion⁽¹¹⁻¹³⁾. The semi-permeable tubing is wrapped around a spindle and the whole unit is enclosed in a shell with openings at both ends for regenerant flow. Wright⁽¹⁰⁾ modified the design by inserting the permeable tubing in another 1.5 mm Teflon tubing. In simple terms, the fibre is constructed of two concentric pieces of tubing. The inner tube is made of sulfonated polyethylene and packed with polymer beads of PS/DVB. The eluent flows through the inner tube while the regenerant flows through the outer tube in the opposite direction. Packing the fibre suppressor with PS/DVB beads is preferred over the unpacked because by changing the flow profile of the eluent, the regeneration is more efficient and the background conductivity is lower. Furthermore, packing reduces the void volume and hence the undesirable band broadening. Although the fibre suppressor is a great improvement over the suppressor column, it still has its limitations - build up of gas bubbles and incompatibility with gradient elution.

Dionex introduced the newest suppressor, the micromembrane suppressor in 1985 and has stopped supplying the fibre suppressor in September 1989. The mechanism is the same as the

fibre suppressor but the construction is new. It is based on "sandwiching" the eluent stream between two regenerant streams. A detail description will be made pending the completion of the study "evaluation of the performance of the anion micromembrane suppressor".

A comparison of the three patented Dionex chemical suppressors is tabulated below.

Feature	Column	Fibre	Micromembrane
Year introduced	1975	1983	1985
Medium	ion exchange resin	ion exchange	semi-permeable membrane
Max. Pressure	highest	200 psi	50 psi
Continuous regeneration	no	yes	yes
Sensitivity	excellent	excellent	excellent
Capacity	high	low	high (10-15 X fibre)
Void volume	2000 μ L	200 μ L	45 μ L
Gradient capability	no	no	yes

Presently we have 8 fibre suppressors and 13 micromembrane suppressors for anion applications. Both devices can be satisfactorily used on any of the instruments.

3.8 Detector

The two most important pieces of equipment in an ion chromatograph are column and detector. While separation in the column is the central issue, the detector is the "eye" which sees the separated components and responds to their presence.

Ideally the detector monitors only the property of the analyte and not the eluent. The cell volume should be small. It should have similar responses to different analytes. The response must be quick, reproducible and linear over a wide concentration range.

The performance of a detector can be further evaluated according to these important properties. First, short-term noise is due to electronic noise which is an intrinsic property. Second, long-term noise is due to malfunctioning of the detector and should be investigated and rectified. Third, drift is due to change in the ambient conditions, especially temperature variation. The magnitude of these three should be as small as possible.

Among the various detectors in IC, the popular ones can be categorized under photometric and electrochemical. The WQS uses only conductometric detection which is one of the electrochemical methods. Since electrical conductivity is a universal property of ionic solutions the choice of conductometric detection seems logical and simple. However the separation of ionic species dictates the use of electrolyte in the eluent and conductivity becomes a bulk property of the eluent. An example is the bicarbonate/carbonate eluent used in our laboratory. As explained in Section 3.7, it is paramount to reduce the conductance of the eluate by chemical suppression in order to improve the signal to background ratio. Having accomplished that, the conductivity detector offers the following advantages.

1. Electrical conductivity is a universal property of ionic solution.
2. At the low concentrations, typical of chromatography, conductivity is proportional to concentration.
3. The detector is simple, robust and quite maintenance free.
4. The cell volume can be miniaturized to reduce void volume.

In a traditional conductivity detector, a sinusoidal alternating voltage is applied across the electrodes. Due to the formation of the electrical double layers at the electrodes, capacitive resistance develops in addition to the simple ohmic resistance. The former causes a shift in the phase of the sine wave and the ohmic resistance cannot be measured with linearity. The bipolar pulse solves this problem. When the capacitance is fully charged, the ohmic resistance is measured digitally. During the negative portion of the pulse, the ionic clouds at the electrodes are discharged with the reversal in polarity.

The detector microprocessor improves the detector performance in the following ways. First, the Dionex detector contains usually a 16-bit processor with an 11-bit analogue to digital (A/D) converter to offset a high signal. The net effect is devoting the 65,536 divisions in the 16-bit processor to the

1-5 μS range, greatly improving the resolution at the low range and consequently allowing detection at the ppb levels. Second, the A/D converter integrates the baseline signal over a fixed time period at constant intervals instead of taking point signals. The result is smoother baseline. Third, the conductivity of an electrolyte solution is a function of temperature. The relationship is given by:

$$C(t) = C(25) e^{k(t-25)}$$

where C(t): Conductivity at temperature t.
C(25): Conductivity at 25°C.
e: Base of natural logarithm.
k: Temperature coefficient (% per °C).
t: Temperature in Celsius.

The experimental term is approximately 1.017. The effect of temperature variation is reduced by normalizing all measured conductivities to 25°C. If the temperature can be measured, the conductivity at any temperature can be calculated by the processor. To achieve this, the detector cell is constructed with a small thermistor hanging in the eluent flow.

The six detectors installed on the older ion chromatographs belong to this type. They are the ORGSO4, PRIC1, PRLOV/PRSEQ and RMDSO4 workstations. Two spares are kept. In the newer models such as the Dionex 4000i, the temperature coefficient is adjustable and can be changed to values other than 1.7%.

3.9 Integrator

Traditionally the integrator measures the elution time and counts the peak area on the chromatogram. With the advent of microprocessor the modern day integrator has become the "brain" of the ion chromatograph. It helps the user to analyze a large number of samples, accumulate a massive set of data, manipulate all the stored information and produce a report. All these are accomplished by electronic circuitry and automation. It enables the laboratory to get more done repetitively and in shorter period of time.

The conductivity detector sends an electric current to the integrator which converts the voltage to the frequency by the V/F converter. During integration, the impulses from the V/F converter are counted at fixed intervals. The model 4270 Integrator used in the IC laboratory uses a 16.6 millisecond cycle. Each cycle produces one bundle of counts. The impulses

from all the bundles under a peak are added and the sum is proportional to the peak area. In this way, a digital integrator can measure the areas produced by signals varying from several microvolts to 1 volt. Thus the linear range covers five orders of magnitude.

Before the introduction of the electronic digital integrators, manual measurement of peak responses by peak height was the most convenient method for quantification. This tradition of peak height measurement has been kept in the IC Laboratory although all the ion chromatographs are equipped with integrators because visually peak heights are easily related to responses on the chart. Furthermore, as reported by Lo⁽¹⁷⁾, peak height measurements are more accurate for peaks which are not completely resolved but not recommended for asymmetrical peaks or peaks with changing symmetry. On the integrator, when peak height is selected, the counts of the highest bundle is displayed and used for calculations.

In addition to processing the chromatographic information, the integrator controls the operation of the injector and the sampler via time functions and through a digital I/O port. The timing and sequence are defined for each workstation individually.

The Model 4270 Integrators are used exclusively in the Laboratory. Although manufactured by Spectra Physics, it can be purchased under the company names of the vendors. It is a dual channel integrator. Even though it has its own algorithms for calibration - external standard, internal standard, normalization, linear regression or quadratic equation, the calculation and manipulation of data are performed by the Direct Computer Input Program (see Section 4). It is also a plotter but this feature is only occasionally used. There are 6 units of the Model 4270 Integrator.

A. Dionex - 1 unit.

It is used at the PRIC1 workstation.

B. Spectra Physics - 1 unit.

It is used at the ORGSO4 workstation.

C. Varian - 4 units.

One unit is used at the PRLOV/PRSEQ workstation (the double workstation definitely requires the dual channel integrator) and another at the RMDSO4 workstation. The other two are kept as spares.

3.10 Recorder

Before the introduction of electronic data processing (integrator and microprocessor), a linear strip chart was the only means to record the response on a chart for calculation and record keeping. For calibration, standard solutions of known concentrations are analyzed to obtain response factors. The concentrations in the unknown samples are calculated by using single point standard, calibration curve of a series of concentrations, or internal standard for correction of matrix effect. The measured quantity can be peak height, peak area by triangulation, peak area by planimeter, or the seldom used method of cutting out the chart paper under the peak and weighing it. Electronic data processing has replaced the recorder because of the additional features discussed in Section 3.9. In the IC Laboratory, the recorder is used for keeping a record of the data and providing a convenient means of evaluating the performance of the ion chromatographic system by the examination of the chromatograms.

The recorder is set at 0.5 or 1 volt full scale to receive the 1 volt signal from the detector. By proper attenuation, peak responses of suitable sizes can be obtained.

Two types of recorders are used.

A. Linear Instruments Corp. - 4 units.

The voltage can be set from 1 mV to 5 V. The Model 585 is a dual pen recorder. Two units are used at the PRLOV/PRSEQ and RMDSO4 workstations, and one unit is used at the spare Model 10 ion chromatograph. The fourth unit is a triple-pen Model 595.

B. Kipp and Zonen - 1 unit.

This Type BD41 unit is also a dual-pen recorder with a voltage range from 10 mV to 1 V.

4. Electronic Data Processing

Computerization has enabled us to increase the analytical speed not only by automation, but also by the collection and manipulation of the data and the subsequent transmission to a central computer for archiving and reporting.

The communication links between the various equipments are shown on page 32.

1. The ion chromatograph produces an analogue signal from the conductivity detector response.
2. The integrator, Model 4270, converts the analogue signal to digital form and collects the responses.
3. The personal computer (PC), Everex Model 1800, stores the "workstation operating routine", captures and manipulates the chromatographic data, and transmits the final results to the central computer.
4. The Laboratory Information System (LIS), a Hewlett-Packard Model HP 3000 computer, registers the submitted samples, places the samples in a LIS Run, matches analytical results to the client submissions, and generates reports to the clients.

4.1 Data Capture

The responses from the Integrator are captured by the Workstation Operating Routine, written in Basic by M. Rawlings and residing on the PC. A back-up copy is kept on tape. When needed, it is loaded from the PC to the Integrator (see Section 4.2.4).

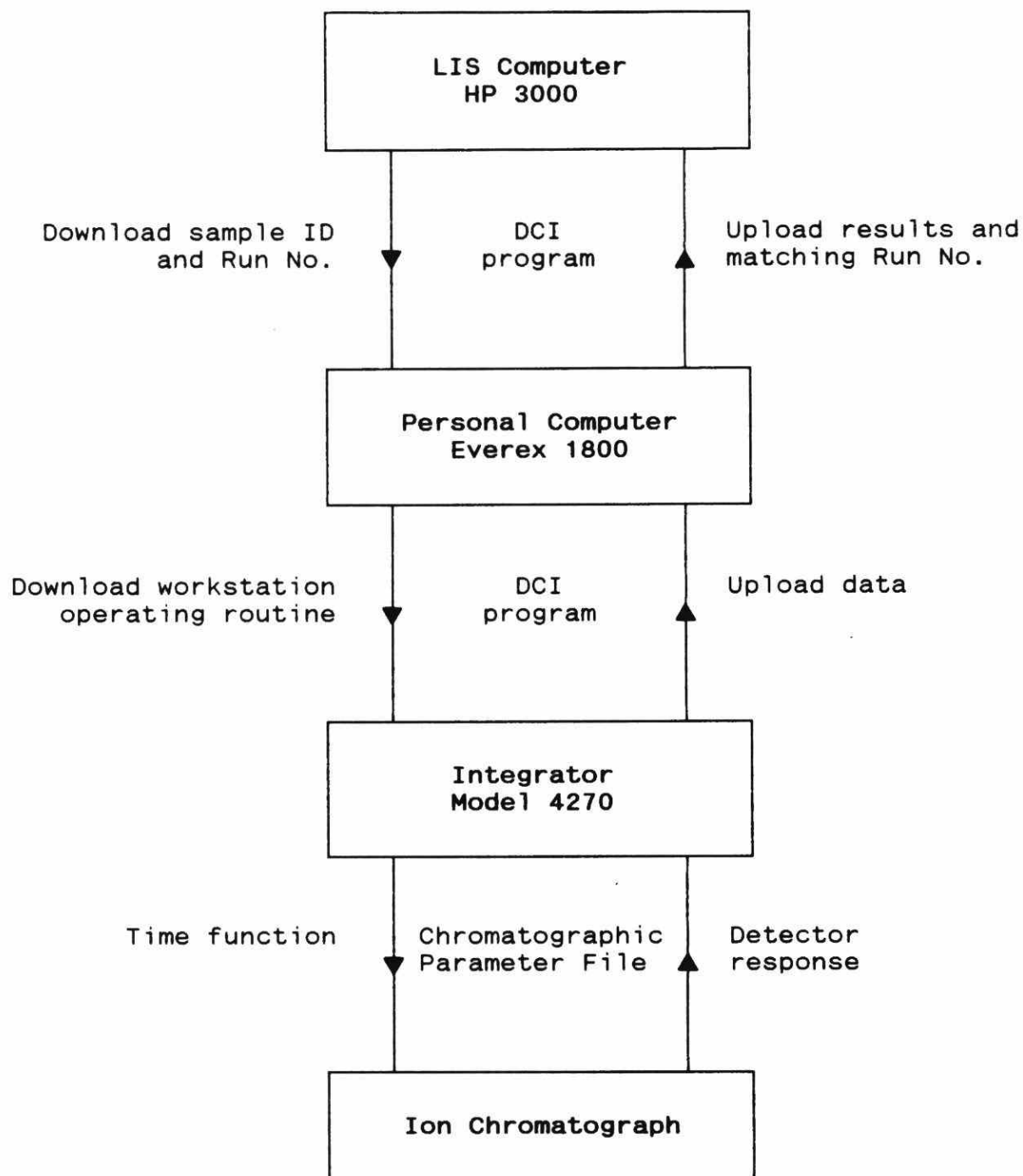
It creates the proper format for the results on the integrator chart, sets the chromatographic parameters, controls the time functions, and stores the peak height counts in an array. One routine is written for each of ORGS04, RMDS04, and PRLOV/PRSEQ workstations.

Since the PRIC1 workstation operates on 3 analytical ranges, 3 files are created and each is individually downloaded when required.

4.2 Data Manipulation and Direct Computer Input

The computer program of the DCI, although not perfect, is both fascinating and impressive. It is a customized software written by a consultant in Clipper for the specific use of the IC Laboratory. Since 1988, it has been maintained and modified by B. Wright. It operates on the PC. The program performs the following functions.

Communication Links Between
LIS Computer and
Ion Chromatograph



- 4.2.1 HP3000/PC Download (Option 1 on Operations Menu).
It allows the user to access the LIS computer and receive the Run. This must be done before analytical data are retrieved from the integrator in step 4.2.5.
- 4.2.2 Run Scheduling (Option 3 on Operations Menu).
It sorts the samples in the LIS Run and put them into a schedule which is an IC Run. The IC Run consists of a header batch and a repetitive body of samples bracketed with In-Run solutions.
- 4.2.3 Run Schedule Adjustment (Option 4 on Operations Menu).
It allows the operator of the workstation to edit (add, delete or change) the information pertaining to the solutions such as the duplicate samples, repeat samples, court case samples, MISA samples and dilution factors in the IC Run.
- 4.2.4 Workstation Start-Up (Option 5 on Operations Menu).
It allows the user to download the "Workstation Operating Routine" that controls the operation of the integrator, interface, injector and sampler.
- 4.2.5 Workstation Response Upload (Option 6 on Operations Menu).
It uploads the analytical data from the integrator to the PC, matching the same positions in the sequence between the IC Run (identified as Workstation Benchsheet) and the integrator chart.
- 4.2.6 Analysis of Data (Choose Analysis on Main Menu).
It evaluates the data of sensitivity, calibration, quality control and duplicates.
- (1) Sensitivity (Option 1 on Analysis Menu).
In-Run (IR) solutions are placed to bracket the calibration solutions, the QC solutions, the duplicate sample solutions and approximately every 10 samples. Since conductivity is dependent on the ambient temperature of the detector, the responses of the bracketed solutions are adjusted proportionally based on the responses of the two IR solutions. If the second IR solution has a higher response than the first, the responses of the bracketed solutions are adjusted lower according to their positions along the sequence inside the bracket. The program also allows the operator to view the graph of all the IR responses.

- (2) Calibration (Option 2 on Analysis Menu).
The conductance response of strong acids such as hydrochloric, nitric and sulfuric is not linear in carbonic acid. As the concentration of a strong acid falls to below 1 M, the rate of drop in conductance decreases. At the higher end of the concentration scale, as the concentration increases, overloading a column leads to peak asymmetry resulting in shorter peaks. The levelling of the calibration response at both ends of the concentration scale produces a sigmoid curve. By using multiple data point calibration, parabolic regression is applied to the data set. The concentrations of chloride, nitrate and sulfate are calculated from their respective responses.
- (3) Quality Control (Option 3 on Analysis Menu).
The results of the QC Solutions A and B, their sum and difference are displayed and evaluated.
- (4) Duplicates (Option 4 on Analysis Menu).
The results of the duplicate pair of the sample are displayed and evaluated.
- (5) Calculated Results (Option 6 on Analysis Menu then Option 1 on Reports Menu).
If the outcome of the evaluations of the QC solutions and duplicate samples is satisfactory, the results of all the solutions including the samples are printed as the "Calculated Results". This is the copy of the final results which can no longer be adjusted.
- 4.2.7 PC/HP3000 Upload (Option 2 on Operations Menu).
It transmits the results from the PC to the LIS according to the LIS Run Numbers for "Run Processing" and "Run Approval". The program matches the individual results with the sample identification.

5. Evaluation of the Ion Chromatographic Systems

An ideal analytical system is not universal. It depends on the requirements placed upon the Laboratory. The factors include capital cost, sample throughput and staffing. In the IC Laboratory, it also depends on the history of the evolution and development of the analytical services. With respect to performance, the key points are specificity, sensitivity, simplicity, speed, and data quality.

5.1 Chemistry

See discussions in Section 5.2.5 - Column and Eluent, and Section 5.2.6 - Suppressor.

5.2 Instrumentation

5.2.1 Eluent Pump

Since a more pulseless eluent flow is preferable, a dual piston pump is a good improvement. It is a standard item in the newer Dionex ion chromatographs, Model 2000i and Model 4000i. The pump should have safety switches and alarms for minimum and maximum pressures.

5.2.2 Sampler

The Gilson x/y/z type (Model 222) should be adopted as the standard because the carousel type is no longer produced. The new type is shared with Atomic Absorption Spectrophotometry Laboratory and Colourimetry Laboratory. The extra desirable features of sample collection and modification to hold two sampling probes have been discussed in Section 3.2.

5.2.3 Peristaltic Pump

Both Technicon proportioning pumps and peristaltic pumps must be kept. The former is necessary for complicated manifolds. The use of one type of pump tubings is a good practice.

5.2.4 Interface

Installing an event marker to produce a negative signal of 50 mV on the recorder chart when the injection valve is switched to the "inject" position makes examination of the chromatogram easier.

5.2.5 Column and Eluent

The low capacity pellicular resin column is preferred over the porous because of its shorter retention and better resolution. The carbonate/bicarbonate eluent has excellent

affinity for the resin and thus is effective in displacing the mono- and di-valent anions. The result is sharper peaks. The concentrations of the electrolytes can be adjusted to manipulate the retention times of chloride, nitrate and sulfate (Section 2.4.4). The ratio of the two can be conveniently changed to achieve desired selectivity. The excellent pH control is discussed in Section 2.4.2. Furthermore, the product after regeneration is dilute carbonic acid and its desirable properties have been discussed in Section 3.7.

Dionex also supplies an AS4A column which is packed with smaller particles. The resins have less cross-linking and lower capacity. The shorter retention time of sulfate by about one-third is impressive but because of its shorter retention and lower capacity, the nitrate and sulfate peaks are closer and the amount of sample loading must be smaller. It is only suitable for samples with low concentrations of narrow range. Its usefulness for precipitation samples and drinking water deserves consideration. Increased back pressure because of its smaller particle size is an undesirable effect.

5.2.6 Suppressor

The advantages of suppressing the eluate conductivity by chemical means and the two types of suppressors have been discussed in Section 3.7. The micromembrane type will eventually replace all the fibre suppressors in the IC Laboratory. Occasionally, claims are made in the IC product literature stating that the need for chemical suppression is eliminated. However the signal to noise ratio must be assessed. In fact the never-ending need for lower detection limits will further entrench the indispensable role of the chemical suppressor.

5.2.7 Detector

Although spectroscopic detector can be used for nitrate and sulfate, a colour producing coupling reagent is required for chloride. Conductivity remains the universal detector for all three anions.

The notorious temperature drift in the IC Laboratory has created two concerns for us. First, the conductivity of the baseline has at times drifted to beyond the bottom end of the chart due to the excessive temperature drop at night. Second, the use of the In-Run solution to correct the change in the responses is a linear function by assuming a linear change in temperature. In reality this may not be so. The microprocessor together with the thermistor can only correct for minor fluctuations in the temperature effect on the detector cell. Insulating the detector such as in the Model 4000i provides more protection.

5.3 Electronic Data Processing

The unique DCI program together with the hardware is a powerful tool. An additional desirable feature is providing a pause in the program after the analysis of the QCA and QCB solutions. This would give the operator time to evaluate the performance of the system before proceeding to the full run instead of "fait accompli".

5.4 Conclusion

The field of analytical chemistry is dynamic and fascinating. Improvements are continually made. Methods for deriving chemical information from a variety of systems and environment have changed dramatically. Unique principles from chemistry, physics and biology are the basis for sophisticated analytical instruments that incorporate computers for data acquisition, manipulation and interpretation. We are dealing with more than the question of "What?" and "How Much?" these days. Analytical systems have been developed and shown orders of magnitude improvements in sensitivity, specificity and speed, and yet with great simplicity and ease. This is the general trend and the latest major invention in "Instrumental Analysis" is Ion Chromatography. Since the inaugural paper of Small in 1975, IC has established itself as an indispensable laboratory tool for a modern analytical chemist.

The present Ion Chromatographic Systems, incorporating parts from various sources and partly developed in-house, are ideally suited for the high sample volume and fast throughput operation of the WQS in the Laboratory Services Branch in support of the many programs requested by various Branches and Agencies. In 1989, we performed approximately 10600 chloride tests, 12000 nitrate tests and 35000 sulfate tests by IC. The design of the systems developed and refined over the years is rugged. Its performance is unaffected by small changes in the procedure when the QA/QC protocol is followed.

We should continue the use of Dionex technologies and parts, Gilson samplers and Technicon proportioning pumps. The adoption of single suppliers within the WQS simplifies purchasing, inventory, and repairs. It also facilitates training of our technical staff.

6. References

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Table I
Retention Time and Response

		Cl	NO ₃	SO ₄
Retention Time (min)	1	2.43	7.44	10.75
	2	2.39	7.39	10.75
	3	2.41	7.42	10.80
	Ave	2.41	7.42	10.77
	%RSD*	0.83	0.34	0.27
Peak height (counts)	1	157896	144044	148276
	2	163765	144406	154911
	3	158981	140493	149109
	Ave	160214	142981	150765
	%RSD*	1.95	1.51	2.40

* %RSD - percent relative standard deviation

Table II
Conductivity and pH of Eluent

% of regular	Concentration		Conductivity (μS/cm)	pH
	M NaHCO ₃	M Na ₂ CO ₃		
80	0.00240	0.00192	626	10.02
85	0.00255	0.00204	662	10.01
90	0.00270	0.00216	699	10.02
95	0.00285	0.00228	727	10.01
100	0.00300	0.00240	762	10.01
105	0.00315	0.00252	799	9.99
110	0.00330	0.00264	833	10.02
115	0.00345	0.00276	870	10.01
120	0.00360	0.00288	908	10.03

Table III
Conductivity of Suppressed Eluate

Conc. of Eluent (% of regular)	Conc. of H_2CO_3 (M)	Suppressed Eluate	
		Conductivity ($\mu\text{S}/\text{cm}$) (Dionex Detector)	Conductivity ($\mu\text{S}/\text{cm}$) (Radiometer)
80	0.00432	11.5	14.6
85	0.00459	11.7	14.8
90	0.00486	12.1	15.4
95	0.00513	12.4	15.5
100	0.00540	12.7	15.7
105	0.00567	13.1	16.3
110	0.00594	13.2	16.5
115	0.00621	13.5	16.8
120	0.00648	14.4	17.4

Table IV
Retention Time and Resolution

Conc. of Eluent (% of regular)	Retention Time (min)			R_s^*
	Cl	NO_3	SO_4	
80	2.17	7.00	11.28	2.25
85	2.13	6.91	10.60	2.02
90	2.13	6.89	9.99	1.74
95	2.03	6.21	9.54	1.95
100	2.00	6.05	9.02	1.82
105	1.99	6.01	8.60	1.65
110	1.97	5.85	8.18	1.62
115	1.94	5.76	7.80	1.46
120	1.91	5.63	7.35	1.33

R_s^* : Resolution between Nitrate and Sulfate peaks.

Figure 1

Chromatogram of standard Operating Conditions

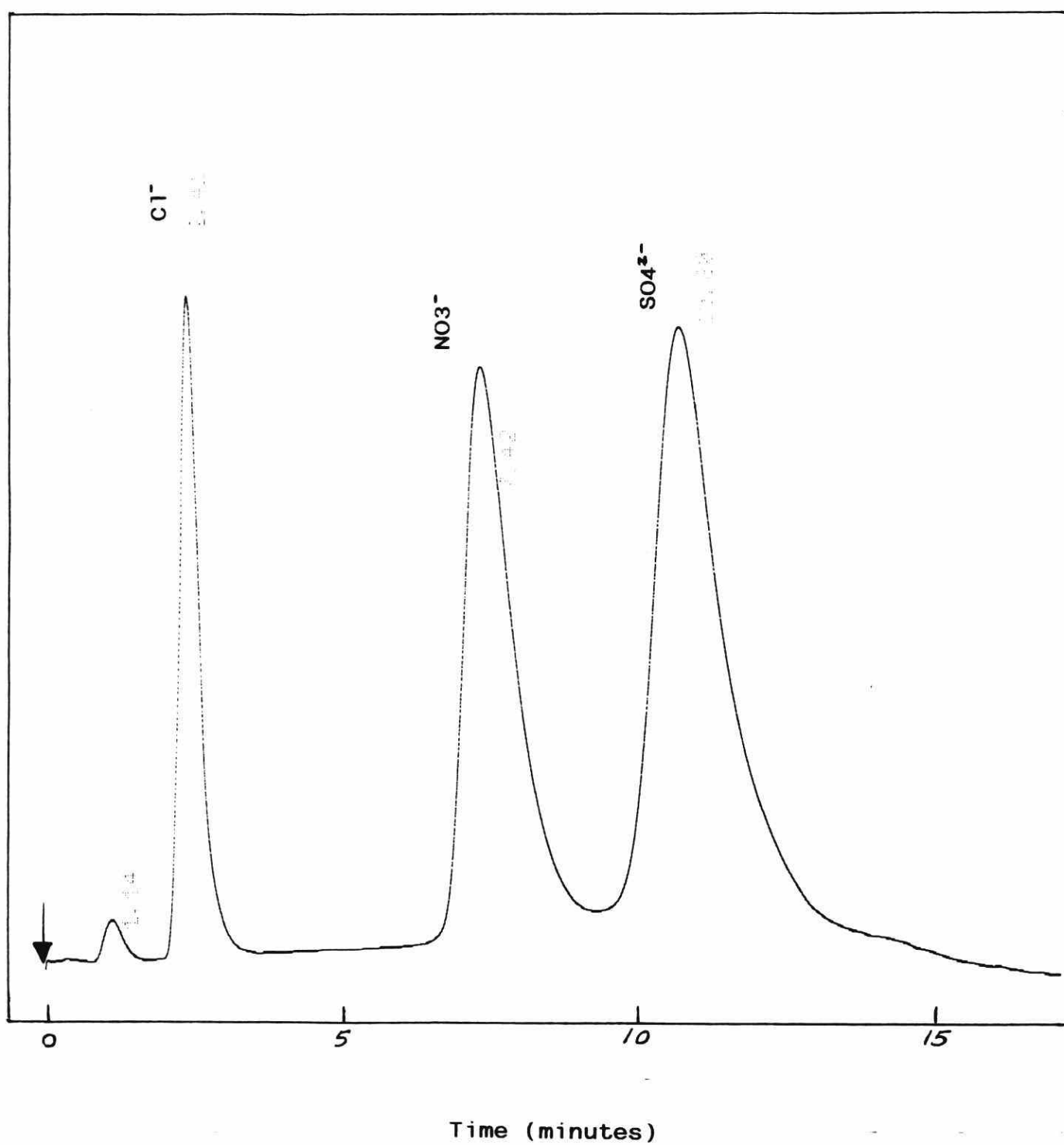


Figure 2

Eluent Concentration and Conductivity

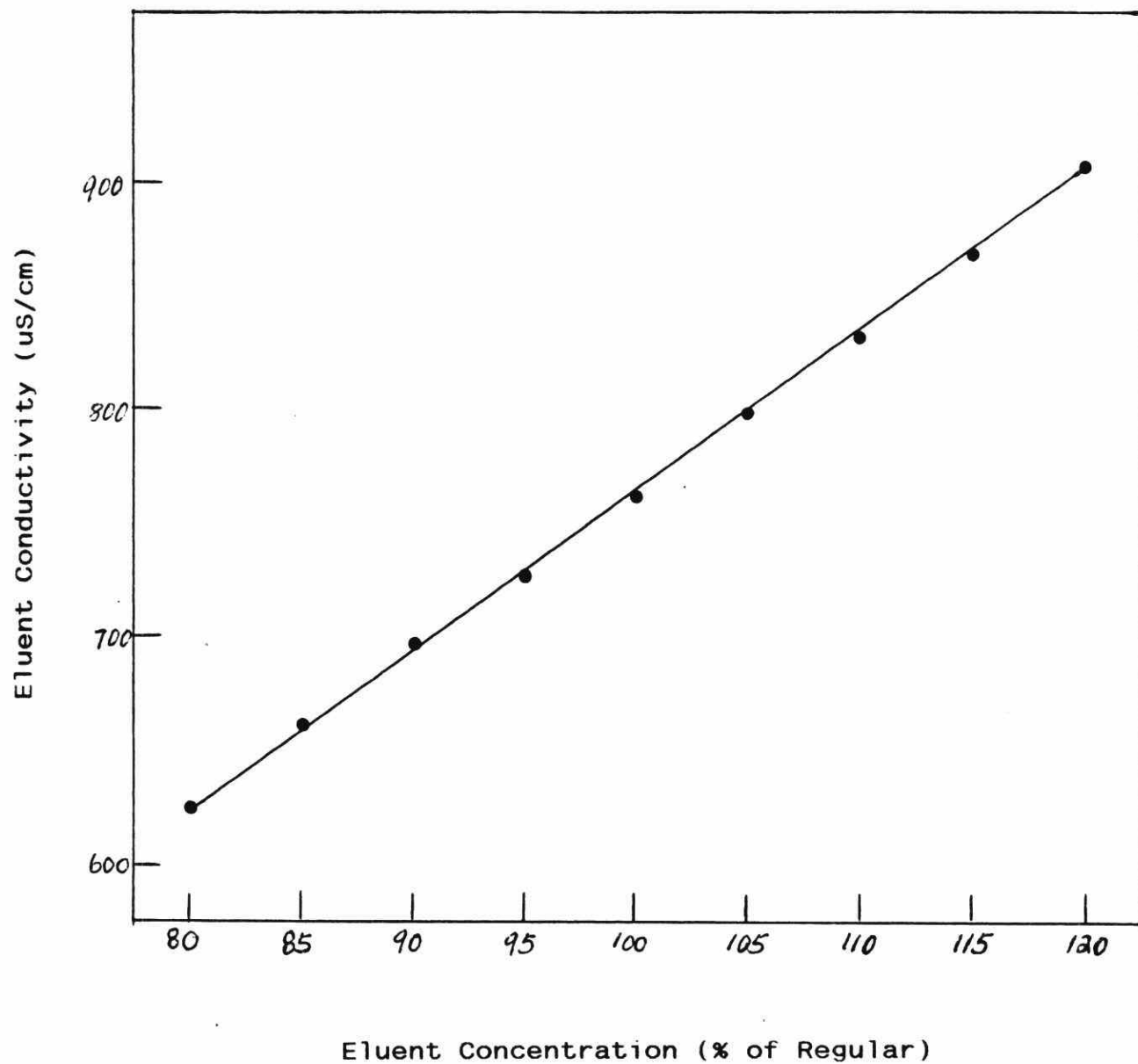


Figure 3

Eluent Concentration and Eluate Conductivity

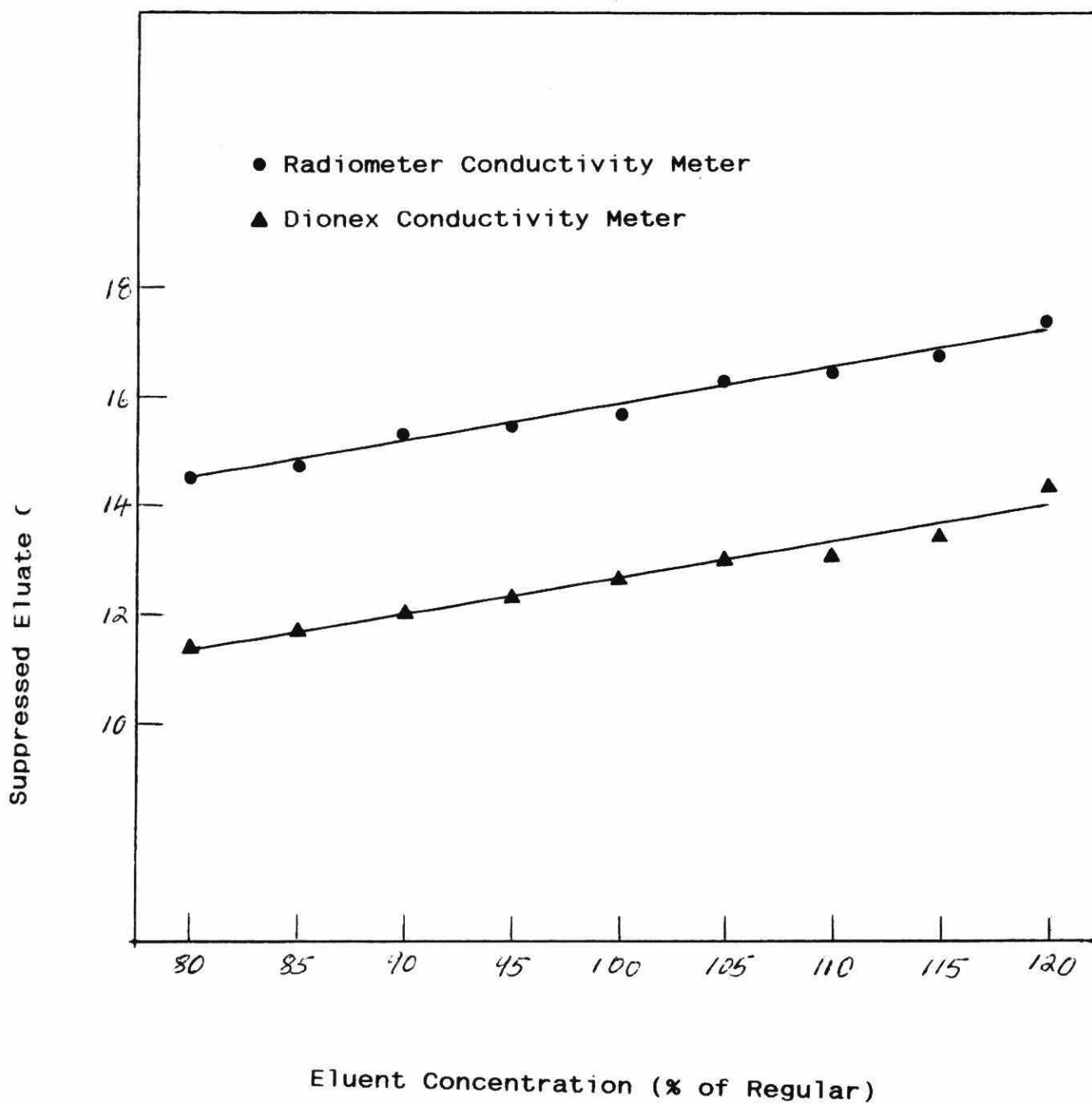


Figure 4.1

Chromatogram of 80% Regular Eluent

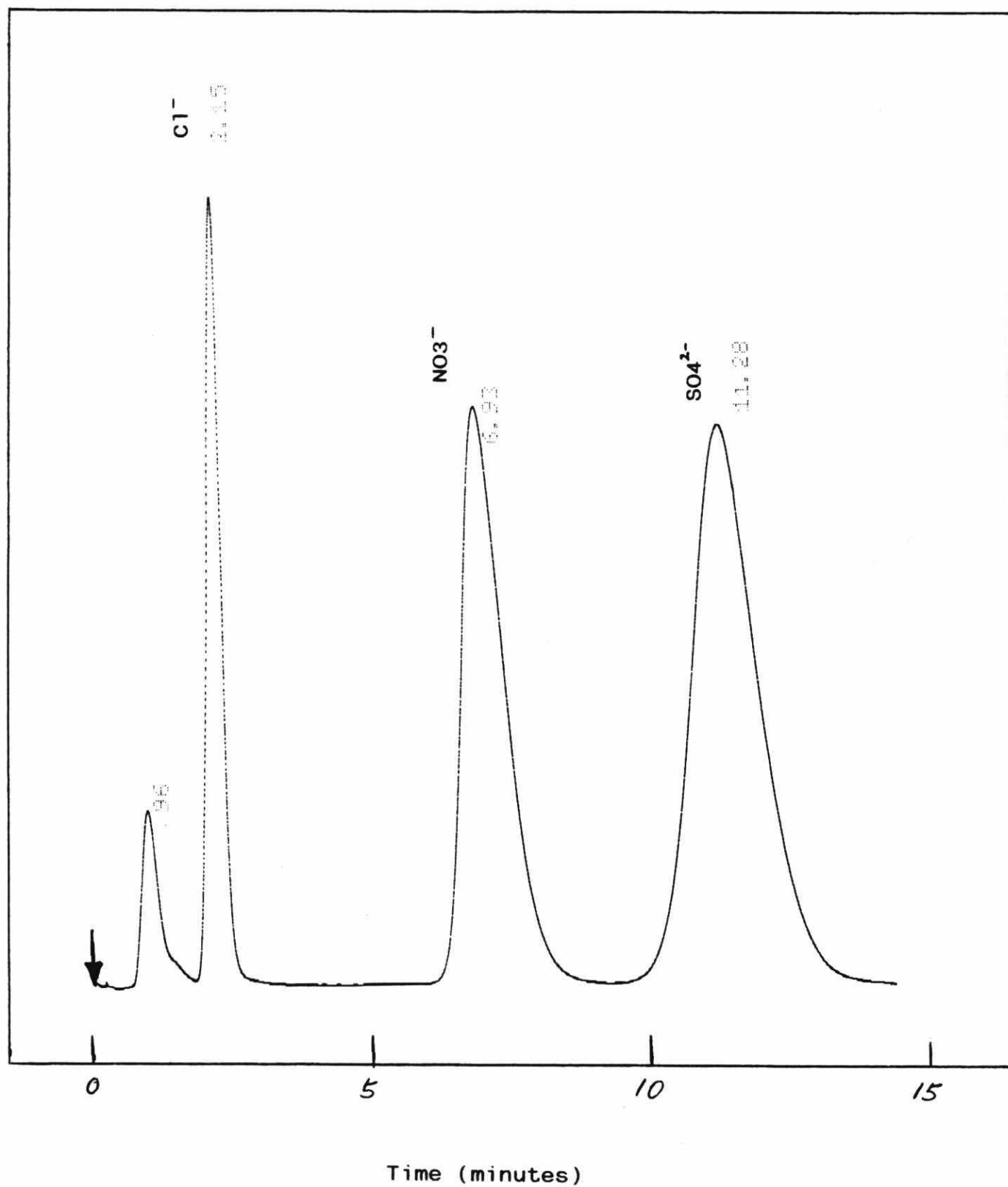


Figure 4.2

Chromatogram of 85% Regular Eluent

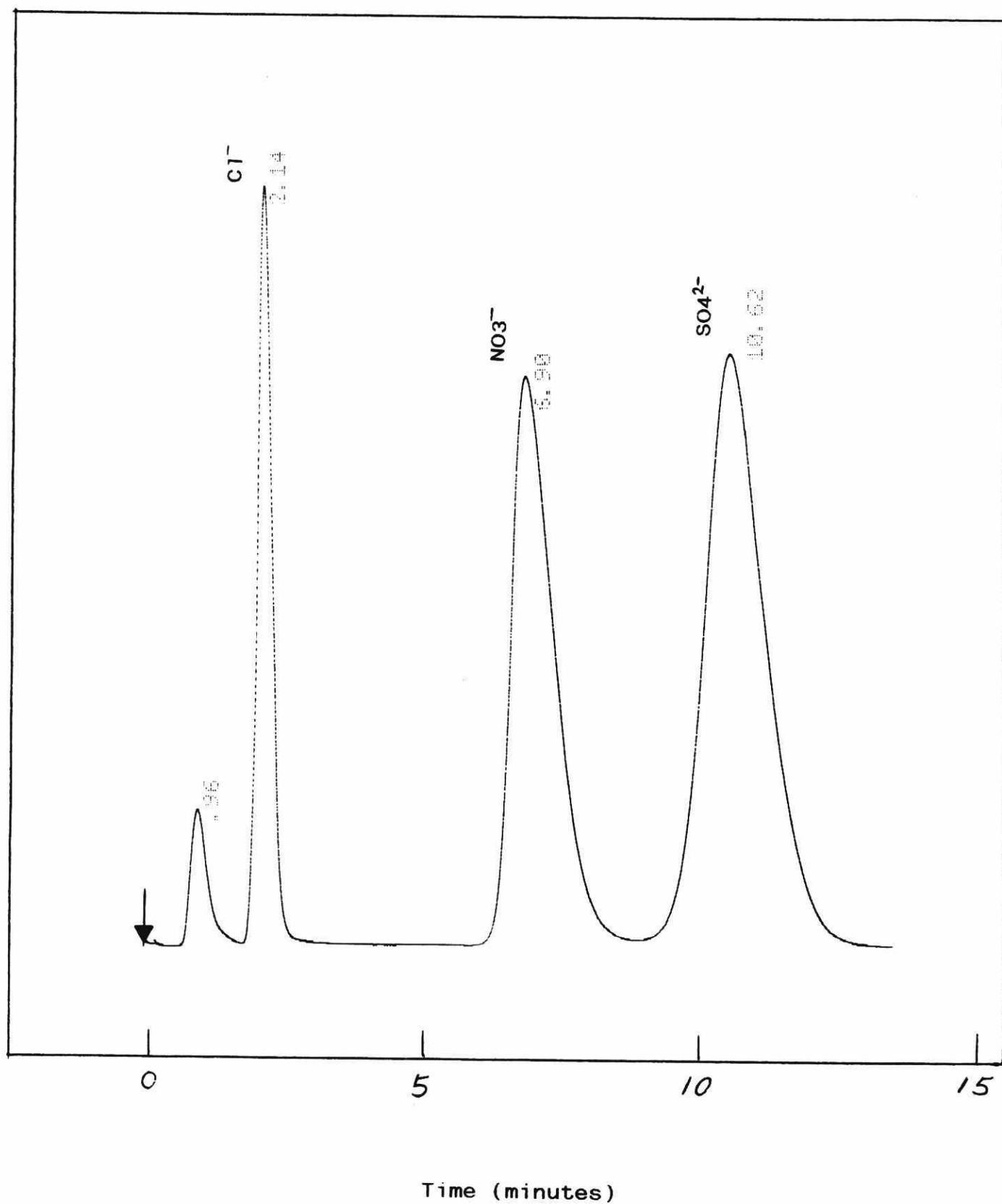


Figure 4.3
Chromatogram of 90% Regular Eluent

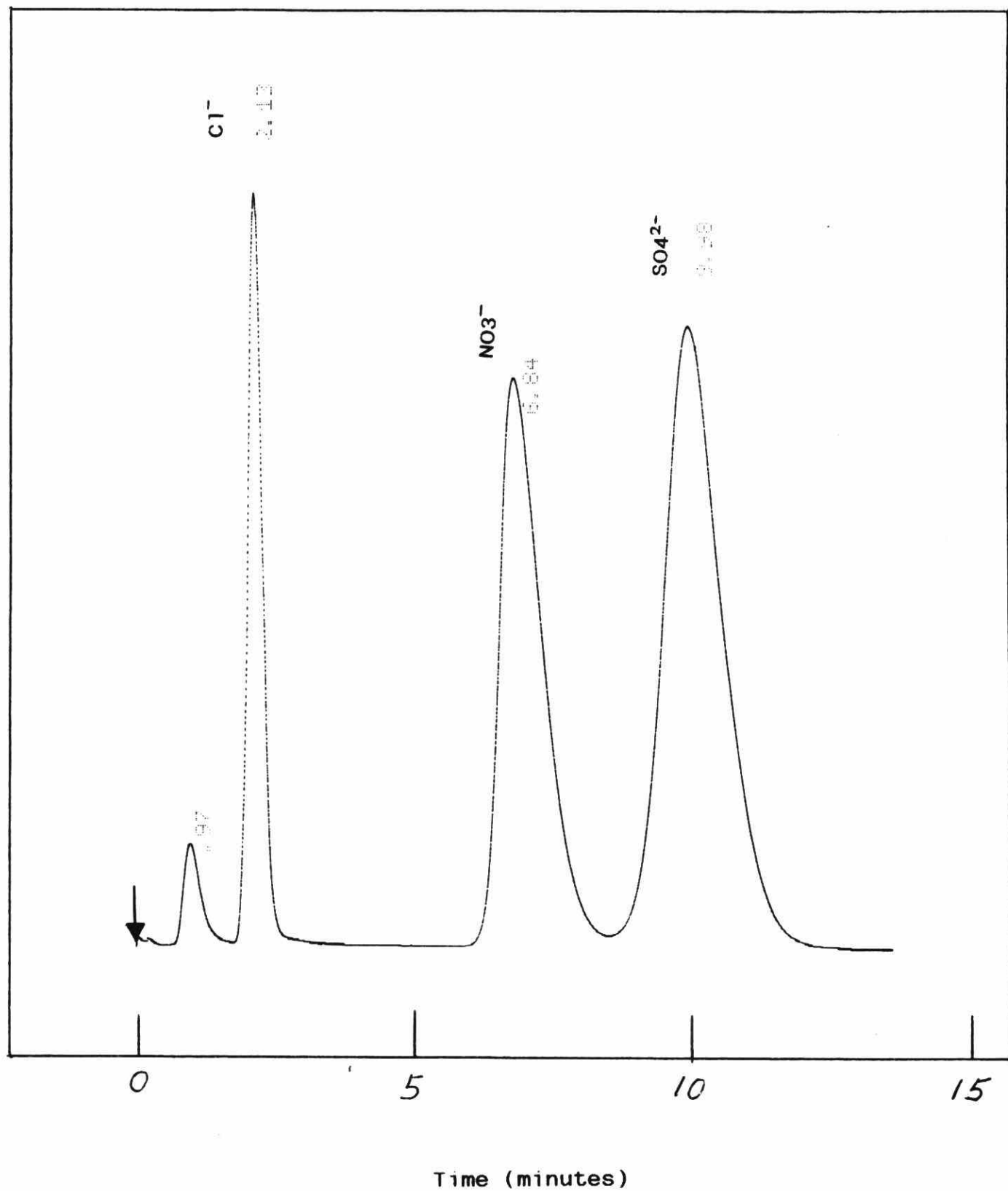


Figure 4.4
Chromatogram of 95% Regular Eluent

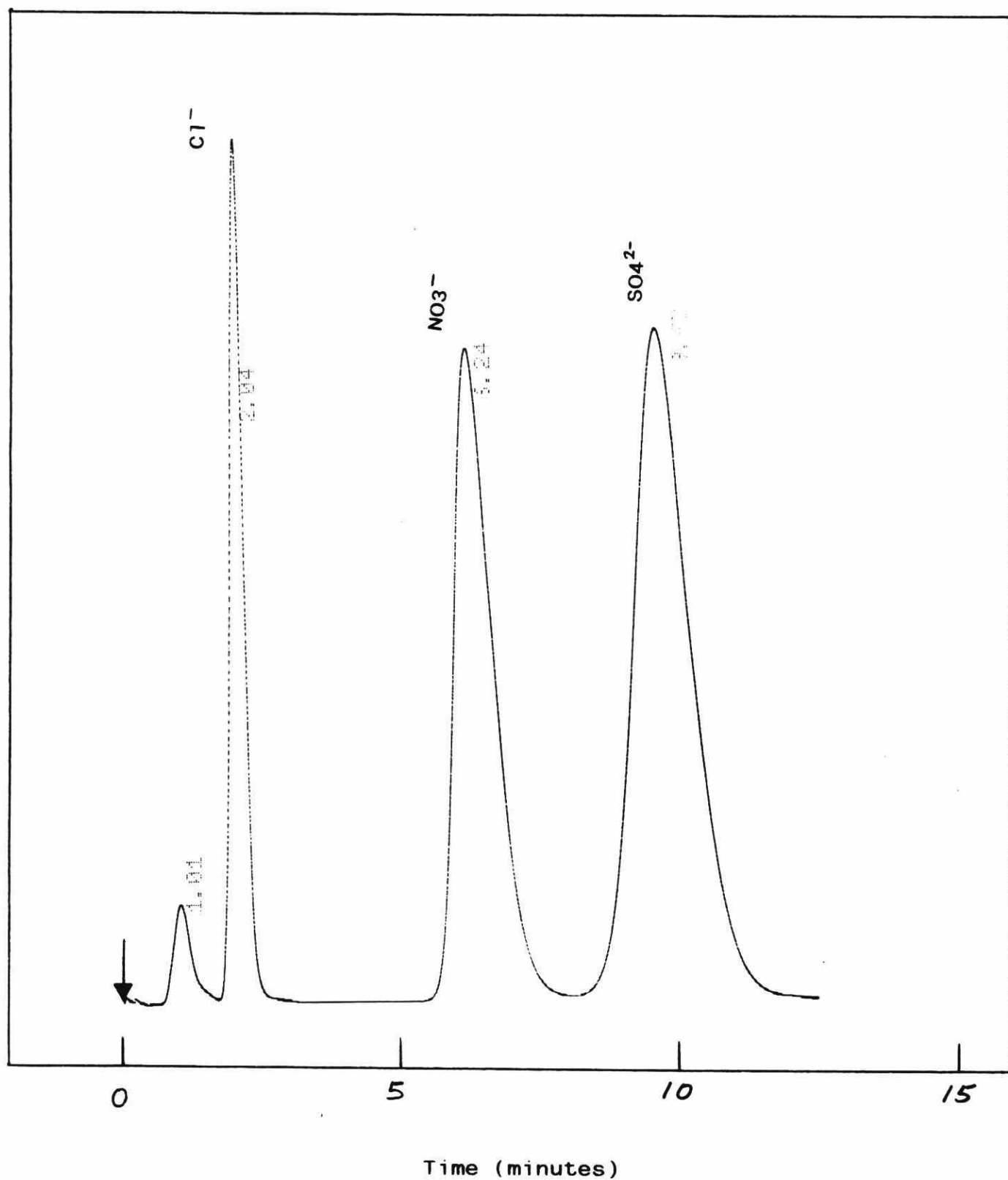


Figure 4.5
Chromatogram of 100% Regular Eluent

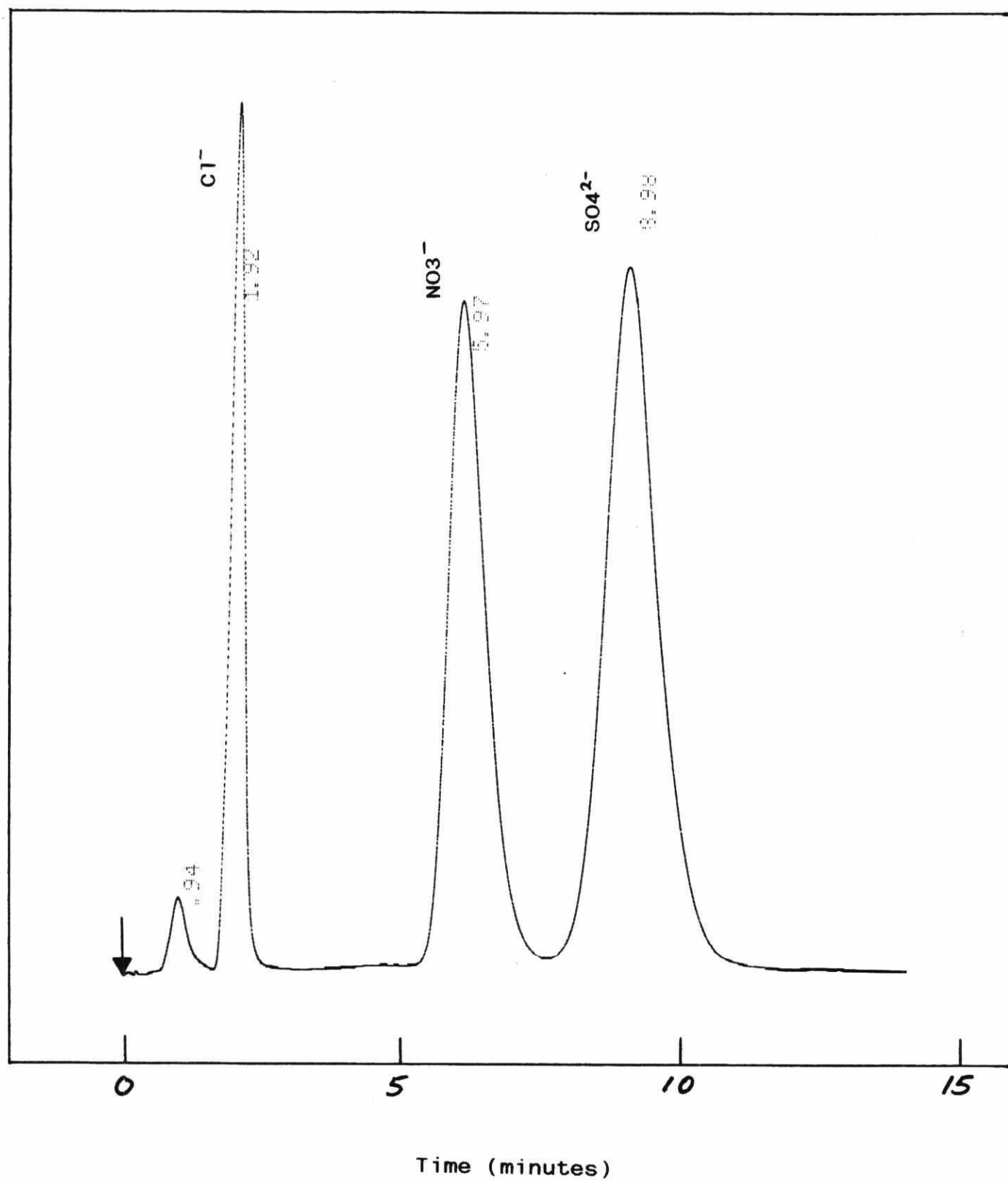


Figure 4.6
Chromatogram of 105% Regular Eluent

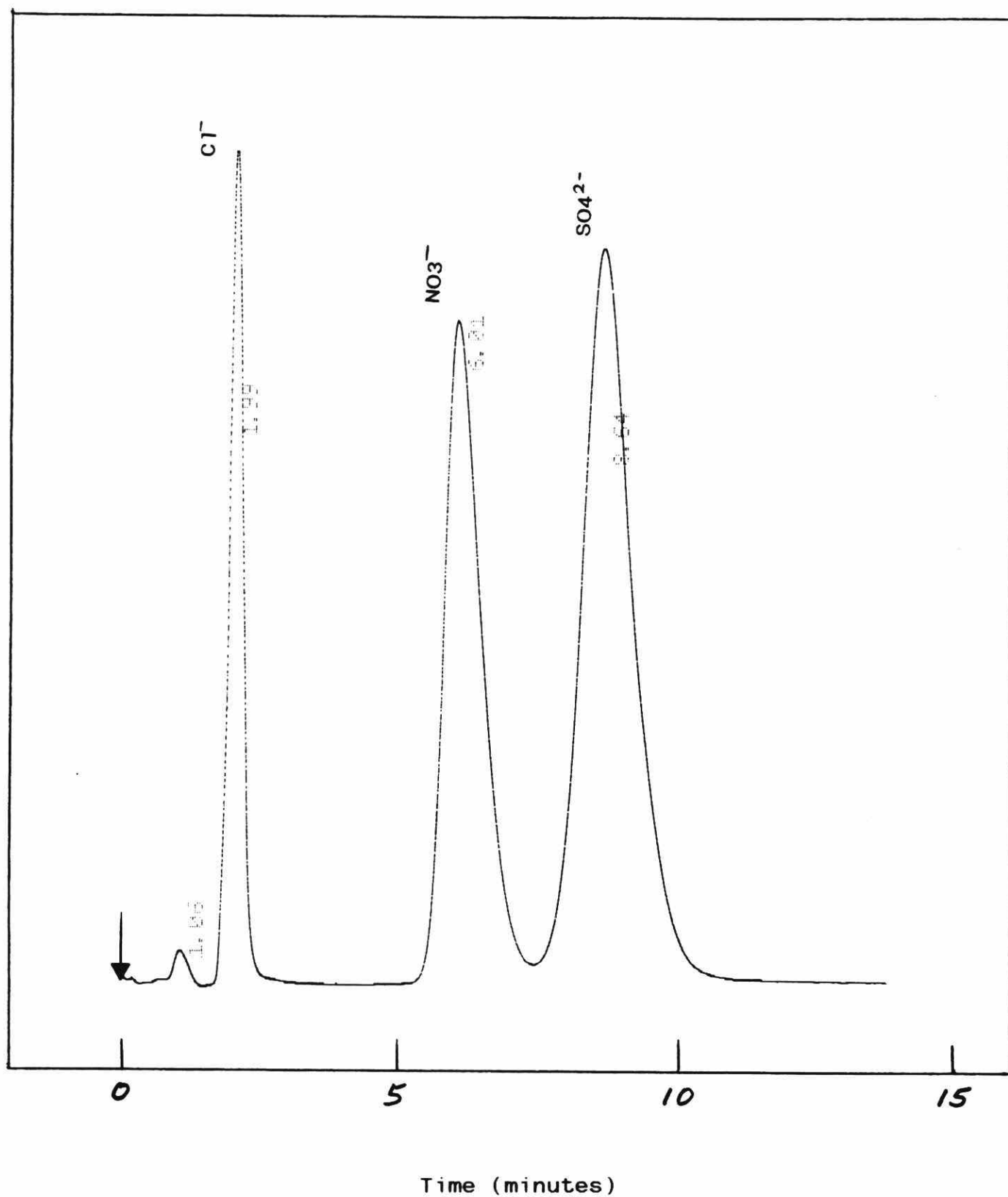


Figure 4.7

Chromatogram of 110% Regular Eluent

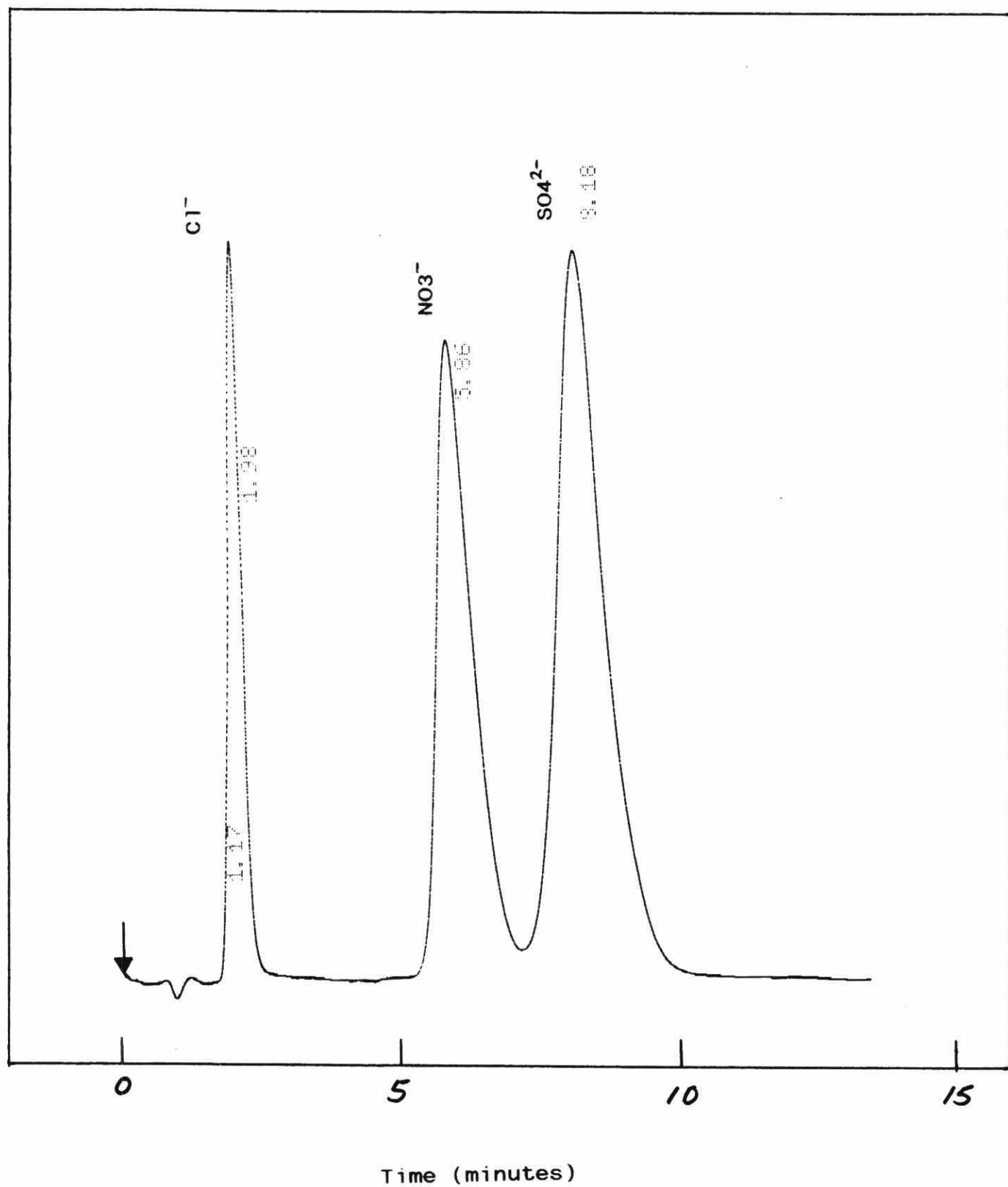


Figure 4.8

Chromatogram of 115% Regular Eluent

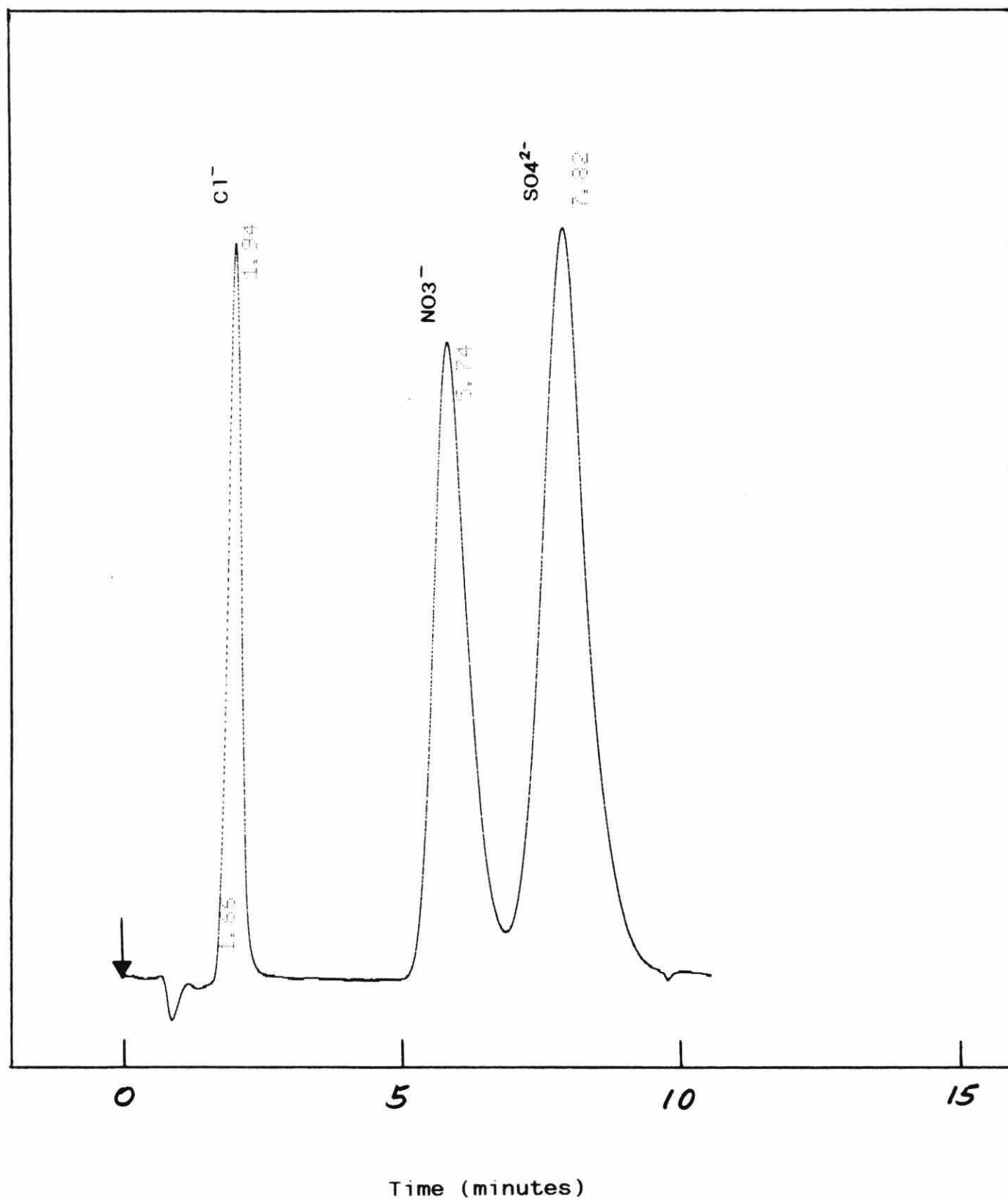


Figure 4.9

Chromatogram of 120% Regular Eluent

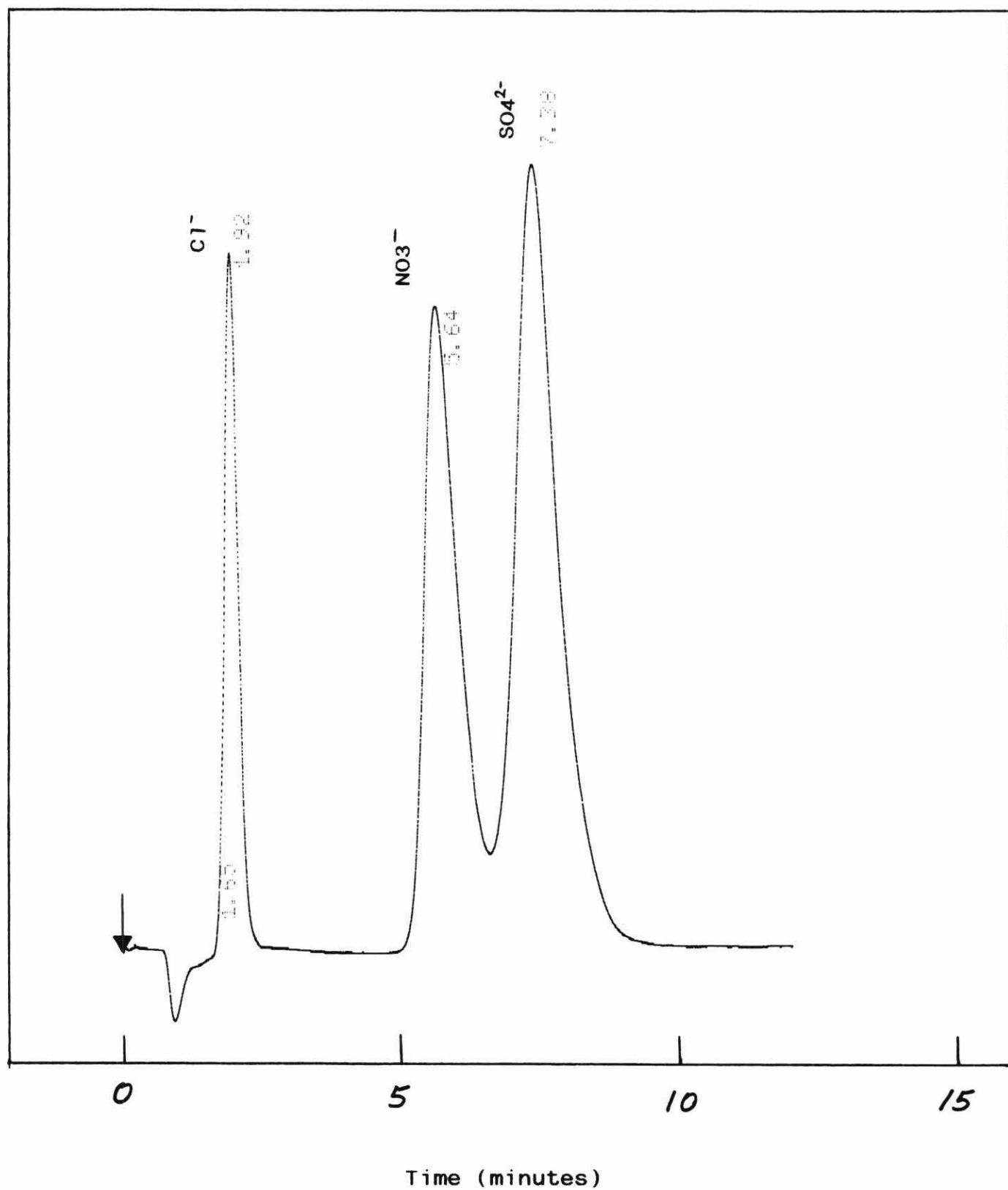


Figure 5
Effect on Retention Time

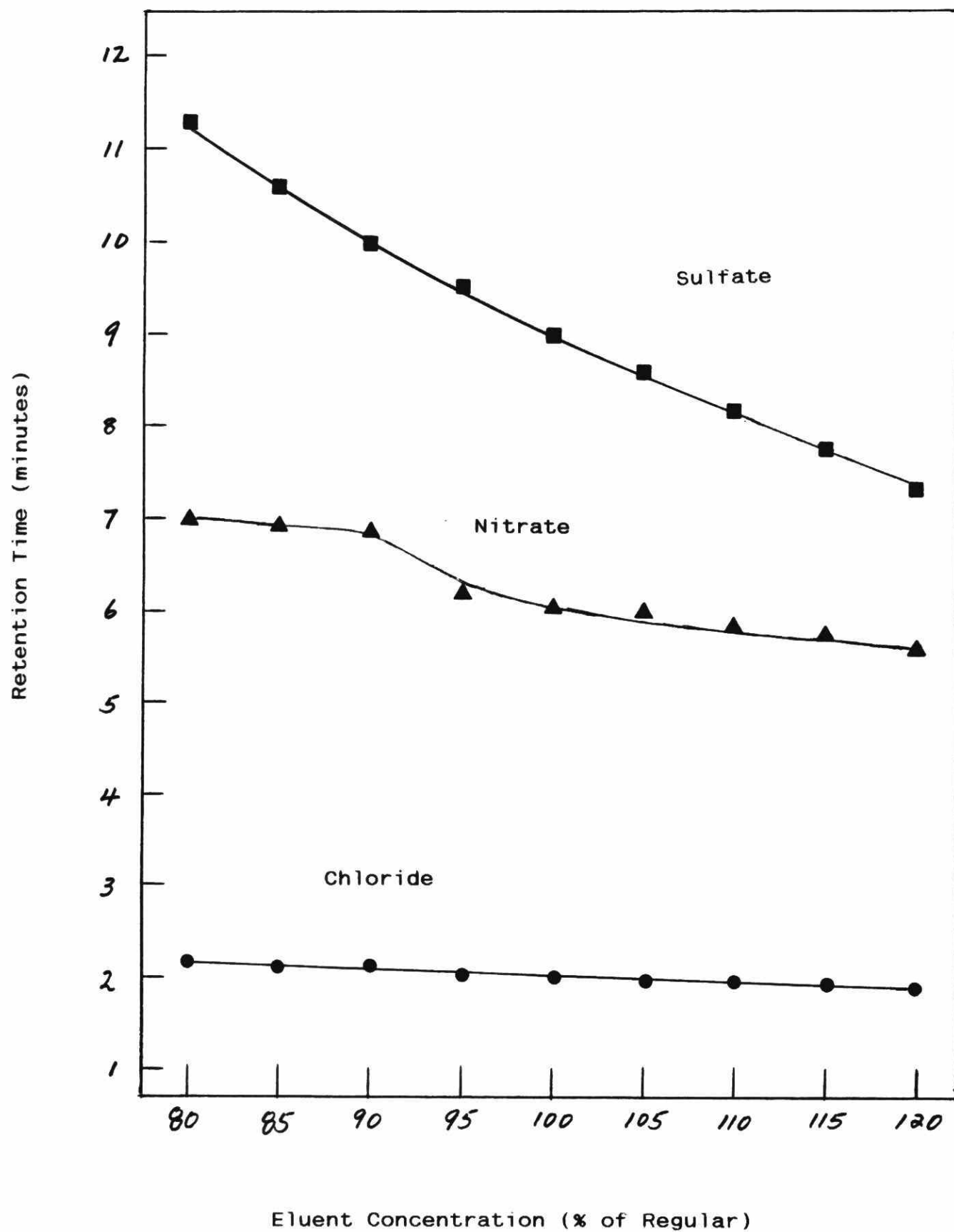


Figure 6
Effect on Resolution

